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Anna R. Maddalena
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Anna R. Maddalena
Signature

7/9/01
Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF
HIDETAKA OKA ET AL

Group Art Unit:
Examiner:

APPLICATION NO: 09/734,635

FILED: DECEMBER 12, 2000

FOR: PHOTSENSITIVE RESIN COMPOSITION

Assistant Commissioner for Patents
Washington, D.C. 20231

CLAIM OF PRIORITY UNDER 35 USC 119

Sir:

Applicants in the above-entitled application by their attorney hereby claim priority under the International Convention of European application Nos. 99811161.1 and 00810630.4, filed on December 15, 1999 and July 17, 2000 respectively. These applications are acknowledged in the Declaration of the instant case.

Certified copies of said European applications are submitted herewith.

Respectfully submitted,

David R. Crichton
David R. Crichton
Attorney for Applicants
Reg. No. 37,300

Ciba Specialty Chemicals Corporation
Patent Department
540 White Plains Road
P.O. Box 2005
Tarrytown, NY 10591-9005
(914) 785-7124
DRC/am/
Encl. (2)



1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes the need for transparency and accountability in financial reporting.

2. The second part of the document outlines the various methods and techniques used to collect and analyze data. It includes a detailed description of the experimental procedures and the statistical analysis performed.

3. The third part of the document presents the results of the study. It includes a series of tables and graphs that illustrate the findings and the trends observed during the experiment.

4. The fourth part of the document discusses the implications of the results and the potential applications of the findings. It also addresses the limitations of the study and suggests areas for future research.

5. The fifth part of the document provides a summary of the key points and conclusions. It reiterates the importance of the study and the need for further investigation in this field.

6. The final part of the document includes a list of references and a bibliography. It cites the works of other researchers and provides a comprehensive overview of the literature related to the study.





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Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99811161.1

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 22/11/00
LA HAYE, LE



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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°: 99811161.1

Anmeldetag:
Date of filing:
Date de dépôt: 15/12/99

Anmelder:
Applicant(s):
Demandeur(s):
Ciba Specialty Chemicals Holding Inc.
4057 Basel
SWITZERLAND

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Photosensitive resin composition

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
G03F7/038, G03F7/031

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

Photosensitive resin composition

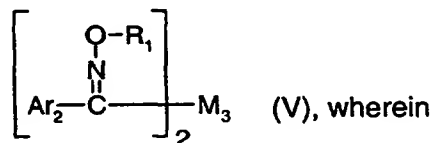
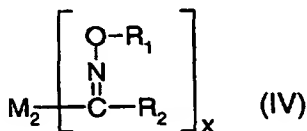
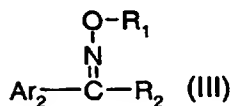
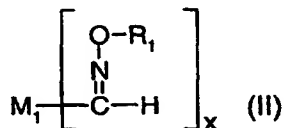
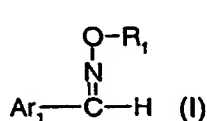
The invention pertains to photosensitive compositions which can be developed by alkali, comprising oxime ester compounds as photoinitiators.

From US patents 3558309, 4202697, 4255513, 4590145 it is known that oxime ester derivatives are photoinitiators. In JP Kokai Hei 8-272095 solder resist ink compositions comprising inter alia 1-phenyl-1,2-propanedione-2-o-benzoyl oxime and 1-phenyl-1,2-propanedione-2-o-ethoxycarbonyl oxime as photoinitiators are disclosed. In JP Kokai Hei 8-339081 in a similar composition 1-phenyl-1,2-propanedione-2-o-ethoxycarbonyl oxime is employed.

In photopolymerization technology there still exists a need for compositions suitable in particular as imaging formulations which are reactive, alkaline developable, easy to handle, exhibit good resolution properties and meet the high requirements of the industry regarding properties like, for example, thermal stability and storage stability.

Surprisingly it was found, that photosensitive compositions comprising

- (A) an oligomer or polymer containing at least one carboxylic acid group in the molecule;
- (B) at least one compound of formula I, II, III, IV or V



R_1 is C_4 - C_9 cycloalkanoyl, C_3 - C_{12} alkenoyl; C_1 - C_{20} alkanoyl which is unsubstituted or substituted by one or more halogen, CN or phenyl; or R_1 is benzoyl which is unsubstituted or substituted by one or more C_1 - C_6 alkyl, halogen, CN, OR_3 , SR_4 or NR_5R_6 ; or R_1 is C_2 - C_{12} alkoxycarbonyl or phenoxy carbonyl which is unsubstituted or substituted by one or more C_1 - C_6 alkyl or halogen;

R_2 is phenyl which is unsubstituted or substituted by one or more C_1 - C_6 alkyl, phenyl, halogen, OR_3 , SR_4 or NR_5R_6 ; or R_2 is C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl; or C_2 -

- 2 -

C₂₀alkyl optionally interrupted by one or more -O- and/or optionally substituted by one or more halogen, OH, OR₃, phenyl or phenyl substituted by OR₃, SR₄ or NR₅R₆; or R₂ is C₃-C₈cycloalkyl, C₂-C₂₀alkanoyl; or benzoyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, phenyl, OR₃, SR₄ or NR₅R₆; or R₂ is C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups; or R₂ is phenoxycarbonyl which is unsubstituted or substituted by C₁-C₆alkyl, halogen, phenyl, OR₃ or NR₅R₆; or R₂ is -CONR₅R₆, CN, NO₂, C₁-C₄haloalkyl, S(O)_mC₁-C₆alkyl, unsubstituted or C₁-C₁₂alkyl-substituted S(O)_m-C₆-C₁₂aryl, SO₂O-C₁-C₆alkyl, SO₂O-C₆-C₁₀aryl, or diphenyl-phosphinoyl, or R₂ may form 5- or 6-membered rings with one of the carbon atoms of the aromatic ring;

m is 1 or 2;

Ar₁ is either C₆-C₂₀aryl or C₆-C₂₀aryloyl,

each of these radicals is unsubstituted or substituted 1 to 12 times by halogen, C₁-C₁₂alkyl, benzyl, benzoyl, C₁-C₁₂alkanoyl, C₃-C₈cycloalkyl; or is substituted by phenyl optionally substituted by one or more OR₃, SR₄ or NR₅R₆; or is substituted by C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆, wherein the substituents OR₃, SR₄ or NR₅R₆ optionally form 5- or 6-membered rings *via* the radicals R₃, R₄, R₅ and/or R₆ with further substituents on the aryl ring of the C₆-C₂₀aryl or C₆-C₂₀aryloyl group or with one of the carbon atoms of the aryl ring of the C₆-C₂₀aryl or C₆-C₂₀aryloyl group;

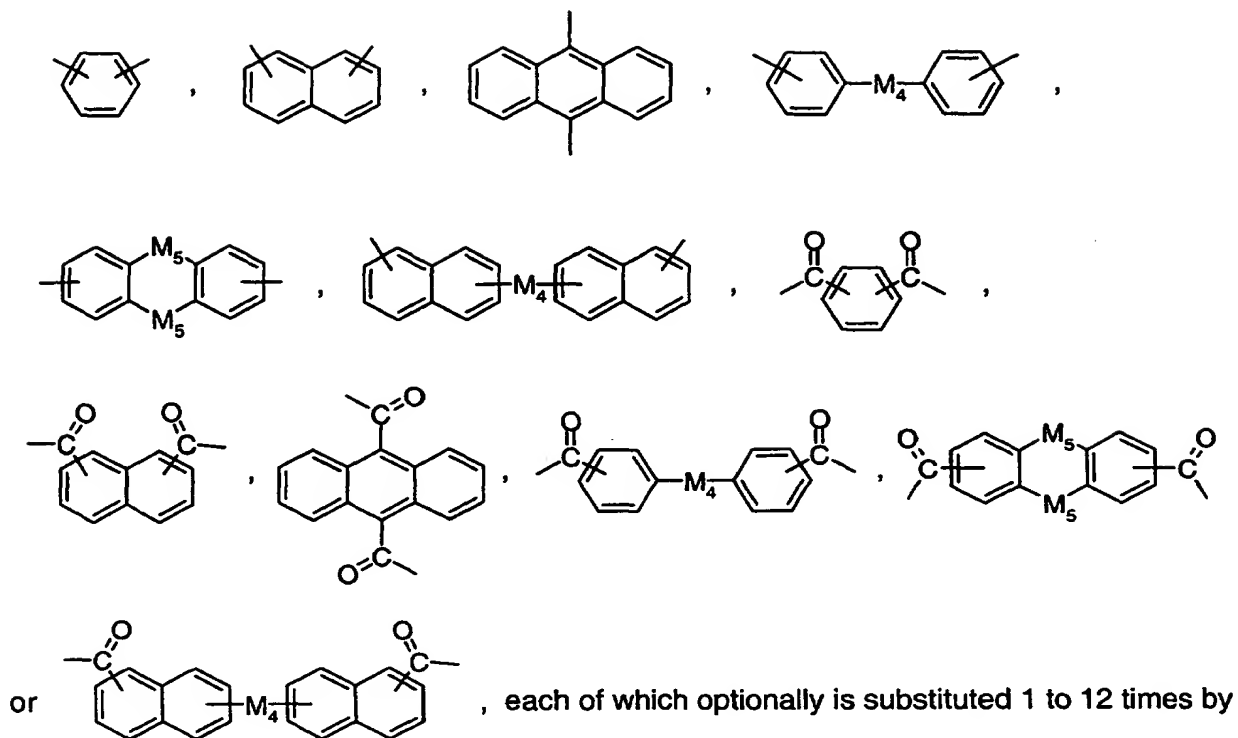
Ar₂ is either C₁₀-C₂₀aryl or C₁₀-C₂₀aryloyl,

each of these radicals is unsubstituted or substituted 1 to 12 times by halogen, C₁-C₁₂alkyl, benzyl, benzoyl, C₁-C₁₂alkanoyl, C₃-C₈cycloalkyl; or is substituted by phenyl optionally substituted by one or more OR₃, SR₄ or NR₅R₆; or is substituted by C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆, wherein the substituents OR₃, SR₄ or NR₅R₆ optionally form 5- or 6-membered rings *via* the radicals R₃, R₄, R₅ and/or R₆ with further substituents on the aryl ring of the C₁₀-C₂₀aryl or the C₁₀-C₂₀aryloyl or with one of the carbon atoms of the aryl ring of the C₁₀-C₂₀aryl or the C₁₀-C₂₀aryloyl;

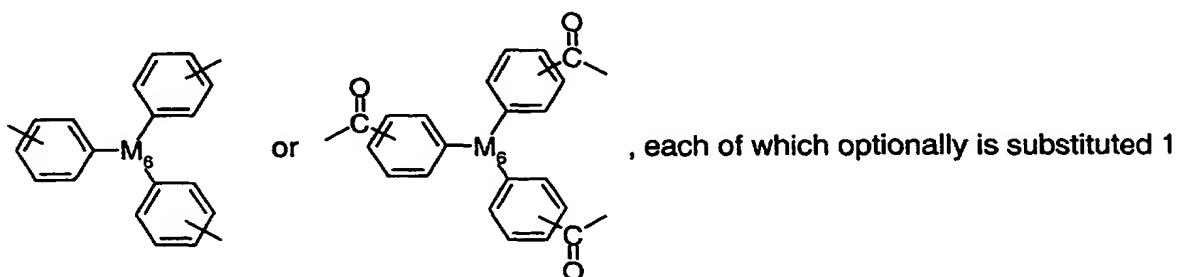
x is 2 or 3;

M₁ when x is 2, is a group

- 3 -



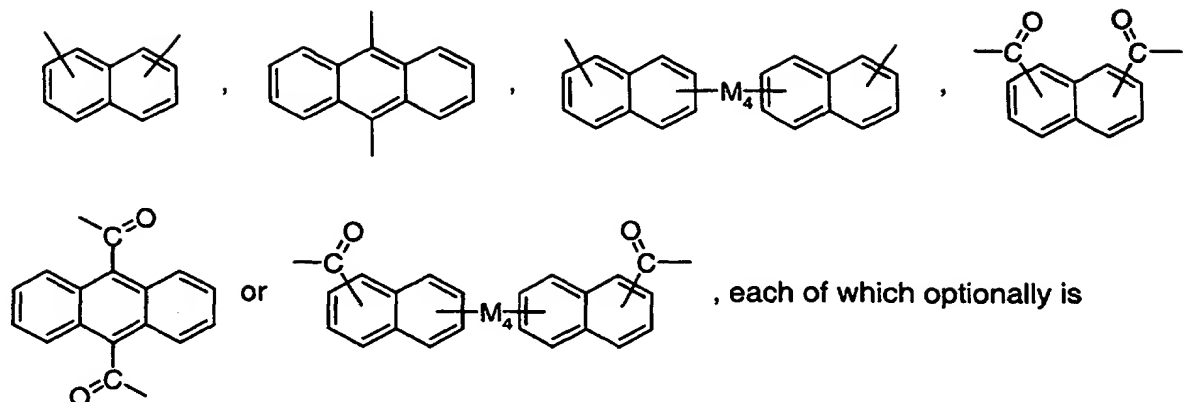
halogen, C₁-C₁₂alkyl, C₃-C₈cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR₃, SR₄ or NR₅R₆; enzy, benzoyl, C₁-C₁₂alkanoyl; C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆;
or M₁, when x is 3, is a group



to 12 times by halogen, C₁-C₁₂alkyl, C₃-C₈cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR₃, SR₄ or NR₅R₆; benzyl, benzoyl, C₁-C₁₂alkanoyl; C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆;

M₂ is a group

- 4 -

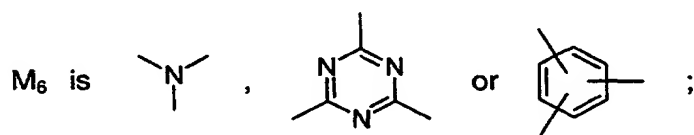


substituted 1 to 8 times by halogen, C_1 - C_{12} alkyl, C_3 - C_8 cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR_3 , SR_4 or NR_5R_6 ; benzyl, benzoyl, C_1 - C_{12} alkanoyl; C_2 - C_{12} alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phenoxy carbonyl or a group OR_3 , SR_4 , SOR_4 , SO_2R_4 or NR_5R_6 ;

M_3 is C_1 - C_{12} alkylene, cyclohexylene, phenylene, $-(CO)O-(C_2-C_{12}alkylene)-O(CO)-$, $-(CO)O-(CH_2CH_2O)_n-(CO)-$ or $-(CO)-(C_2-C_{12}alkylene)-(CO)-$;

M_4 is a direct bond, -O-, -S-, -SS-, $-NR_3-$, $-(CO)-$, C_1 - C_{12} alkylene, cyclohexylene, phenylene, naphthylene, $-(CO)O-(C_2-C_{12}alkylene)-O(CO)-$, $-(CO)O-(CH_2CH_2O)_n-(CO)-$ or $-(CO)-(C_2-C_{12}alkylene)-(CO)-$; or M_4 is C_4 - C_{12} alkylene or C_4 - C_{12} alkylenedioxy-, each of which is optionally interrupted by 1 to 5 -O-, -S- and/or $-NR_3-$;

M_5 is a direct bond, $-CH_2-$, -O-, -S-, -SS-, $-NR_3-$ or $-(CO)-$;



R_3 is hydrogen or C_1 - C_{12} alkyl; or R_3 is C_2 - C_6 alkyl which is substituted by -OH, -SH, -CN, C_1 - C_4 alkoxy, C_3 - C_6 alkenoxy, $-OCH_2CH_2CN$, $-OCH_2CH_2(CO)O(C_1-C_4alkyl)$, $-O(CO)-C_1-C_4alkyl$, $-O(CO)-phenyl$, $-(CO)OH$ or $-(CO)O(C_1-C_4alkyl)$; or R_3 is C_2 - C_6 alkyl which is interrupted by one or more -O-; or R_3 is $-(CH_2CH_2O)_nH$, C_1 - C_8 alkanoyl, C_3 - C_{12} alkenyl, C_3 - C_6 alkenoyl, C_3 - C_8 cycloalkyl; or R_3 is benzoyl which is unsubstituted or substituted by one or more C_1 - C_6 alkyl, halogen, -OH or C_1 - C_4 alkoxy; or phenyl which is unsubstituted or substituted by halogen, -OH, C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_3 is phenyl- C_1 - C_3 alkyl, $Si(C_1-C_6alkyl)_r(phenyl)_{3-r}$;

r is 0, 1, 2 or 3;

R_4 is hydrogen, C_1 - C_{12} alkyl, C_3 - C_{12} alkenyl, cyclohexyl; C_2 - C_6 alkyl which is substituted by -OH, -SH, -CN, C_1 - C_4 alkoxy, C_3 - C_6 alkenoxy, $-OCH_2CH_2CN$, $-OCH_2CH_2(CO)O(C_1-C_4alkyl)$, $-O(CO)-C_1-C_4alkyl$, $-O(CO)-phenyl$, $-(CO)OH$ or $-(CO)O(C_1-C_4alkyl)$; or R_4 is C_2 - C_{12} alkyl which is interrupted by one or more -O- or -S-; or R_4 is phenyl which is unsubstituted or substituted by halogen, C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_4 is phenyl- C_1 - C_3 alkyl;

R_5 and R_6 independently of each other are hydrogen, C_1 - C_{12} alkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_{10} alkoxyalkyl, C_3 - C_5 alkenyl, C_3 - C_8 cycloalkyl, phenyl- C_1 - C_3 alkyl, C_1 - C_4 alkanoyl, C_3 - C_6 alkanoyl, benzoyl or phenyl which is unsubstituted or substituted by C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_5 and R_6 together are C_2 - C_6 alkylene optionally interrupted by -O- or - NR_3 - and/or optionally substituted by hydroxyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoyloxy or benzoyloxy; provided that the compounds

1-naphthyl methyl ketone oxime-O-acetate, 2-naphthyl methyl ketone oxime-O-acetate, 2-naphthyl phenyl ketone oxime-O-propylcarbonate, 9-anthryl methyl ketone oxime-O-acetate, 2-naphthyl methyl ketone oxime-O-benzoate are excluded; and

(C) a photopolymerizable reactive and/or unreactive diluent, exhibit an unexpectedly good performance.

C_1 - C_{20} alkyl is linear or branched and is, for example, C_1 - C_{18} -, C_1 - C_{14} -, C_1 - C_{12} -, C_1 - C_8 -, C_1 - C_6 - or C_1 - C_4 alkyl or C_4 - C_{12} - or C_4 - C_8 alkyl. Examples are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, 2,4,4-trimethylpentyl, 2-ethylhexyl, octyl, nonyl, decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl and icosyl.

C_1 - C_{12} alkyl, C_1 - C_6 alkyl, C_2 - C_6 alkyl and C_1 - C_4 alkyl have the same meanings as given above for C_1 - C_{20} alkyl up to the corresponding number of C-atoms.

C_2 - C_{20} alkyl which is interrupted by one or more -O- is for example interrupted 1-9, 1-5, 1-3 or once or twice by -O-. Two O-atoms are separated by at least two methylene groups, namely ethylene. The alkyl groups are linear or branched. For example the following structural units will occur, $-CH_2CH_2OCH_2CH_3$, $-[CH_2CH_2O]_yCH_3$, wherein $y = 1-9$, $-(CH_2CH_2O)_7CH_2CH_3$, $-CH_2CH(CH_3)OCH_2CH_2CH_3$ or $-CH_2CH(CH_3)OCH_2CH_3$. C_2 - C_6 alkyl which is interrupted by 1 or 2 -O- is for example $-CH_2CH_2OCH_2CH_2OCH_2CH_3$ or $-CH_2CH_2OCH_2CH_3$.

C_2 - C_4 hydroxyalkyl means C_2 - C_4 alkyl, which substituted by one or two O-atoms. The alkyl radical is linear or branched. Examples are 2-hydroxyethyl, 1-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-hydroxybutyl, 4-hydroxybutyl, 2-hydroxybutyl, 3-hydroxybutyl, 2,3-dihydroxypropyl, or 2,4-dihydroxybutyl.

C₃-C₈cycloalkyl is for example cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, especially cyclopentyl and cyclohexyl.

C₁-C₄alkoxy is linear or branched, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, sec-butyloxy, isobutyloxy, tert-butyloxy.

C₂-C₁₀alkoxyalkyl is C₂-C₁₀alkyl, which is interrupted by one O-atom. C₂-C₁₀alkyl has the same meanings as given above for C₁-C₂₀alkyl up to the corresponding number of C-atoms. Examples are methoxymethyl, methoxyethyl, methoxypropyl, ethoxymethyl, ethoxyethyl, ethoxypropyl, propoxymethyl, propoxyethyl, propoxypropyl.

C₁-C₂₀alkanoyl is linear or branched and is, for example, C₂-C₁₈-, C₂-C₁₄-, C₂-C₁₂-, C₂-C₈-, C₂-C₆- or C₂-C₄alkanoyl or C₄-C₁₂- or C₄-C₈alkanoyl. Examples are formyl, acetyl, propionyl, butanoyl, isobutanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, dodecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, octadecanoyl, icosanoyl, preferably acetyl. C₁-C₁₂alkanoyl, C₁-C₈alkanoyl, C₁-C₄alkanoyl and C₂-C₄alkanoyl have the same meanings as given above for C₂-C₂₀alkanoyl up to the corresponding number of C-atoms.

C₄-C₉cycloalkanoyl is for example cyclopropanoyl, cyclobutanoyl, cyclopentanoyl, cyclohexanoyl, cyclooctanoyl.

C₂-C₄alkanoyloxy is linear or branched, for example acetyloxy, propionyloxy, butanoyloxy, isobutanoyloxy, preferably acetyloxy.

C₂-C₁₂alkoxycarbonyl is a linear or branched and is, for example, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, n-butyloxycarbonyl, isobutyloxycarbonyl, 1,1-dimethylpropoxycarbonyl, pentyloxycarbonyl, hexyloxycarbonyl, heptyloxycarbonyl, octyloxycarbonyl, nonyloxycarbonyl, decyloxycarbonyl or dodecyloxycarbonyl, especially methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, n-butyloxycarbonyl or isobutyloxycarbonyl, preferably methoxycarbonyl.

C₂-C₁₂alkoxycarbonyl which is interrupted by one or more -O- is linear or branched. Two O-atoms are separated by at least two methylene groups, namely ethylene.

C₆-C₂₀aryl is for example phenyl, 1-naphthyl, 2-naphthyl, 9-anthryl, 9-phenanthryl, 1-pyrenyl, 2-pyrenyl, 1-perylenyl or 3-perylenyl, preferably phenyl or naphthyl.

C₁₀-C₂₀aryl and C₆-C₁₂aryl have the same meanings as given above for C₆-C₂₀aryl up to the corresponding number of C-atoms.

C₆-C₂₀aryloyl is for example benzoyl, 1-naphthoyl, 2-naphthoyl, 9-anthracenecarbonyl, 9-phenanthrenecarbonyl, 1-pyrenecarbonyl, 2-pyrenecarbonyl, 1-perylenecarbonyl or 3-perylenecarbonyl, preferably benzoyl or naphthoyl.

C₁₀-C₂₀aryloyl has the same meanings as given above for C₆-C₂₀aryloyl up to the corresponding number of C-atoms.

Phenoxycarbonyl is . Substituted phenoxycarbonyl radicals are substituted

one to four times, for example one, two or three times, especially two or three times. Substituents on the phenyl ring are preferably in positions 4 or in 3,4-, 3,4,5-, 2,6-, 2,4- or 2,4,6-position on the phenyl ring, in particular in 4- or 3,4-position.

Phenyl-C₁-C₃alkyl is for example benzyl, phenylethyl, α-methylbenzyl or α,α-dimethylbenzyl, especially benzyl.

C₂-C₂₀alkenyl radicals may be mono or polyunsaturated and are for example C₂-C₁₂-, C₂-C₆-alkenyl, e.g. allyl, methallyl, 1,1-dimethylallyl, 1-butenyl, 3-butenyl, 2-butenyl, 1,3-pentadienyl, 5-hexenyl, 7-octenyl or dodecenyl, tetradecenyl, pentadecenyl, hexadecenyl, octadecenyl and icosenyl especially allyl.

C₃-C₁₂alkenyl radicals and C₃-C₅alkenyl radicals have the same meanings as given above for C₂-C₂₀alkenyl radicals up to the corresponding number of C-atoms.

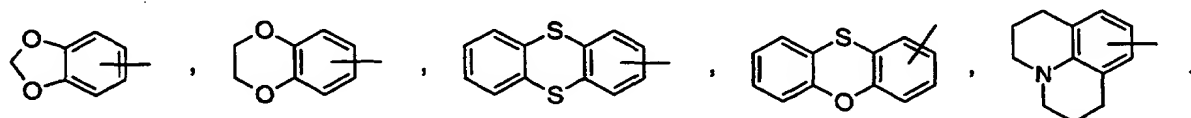
C₂-C₂₀alkynyl radicals are for example C₂-C₁₂-, C₂-C₆-alkynyl and may be mono or polyunsaturated and are for example ethynyl, propargyl, 1-butylnyl, 3-butylnyl, 2-butylnyl, 5-hexynyl, 7-octynyl or dodecynyl, tetradecynyl, pentadecynyl, hexadecynyl, octadecynyl or icosynyl.

C₃-C₆alkenoxy radicals may be mono- or polyunsaturated and are for example allyloxy, methallyloxy, butenyloxy, pentenoxy, 1,3-pentadienyloxy, 5-hexenyloxy.

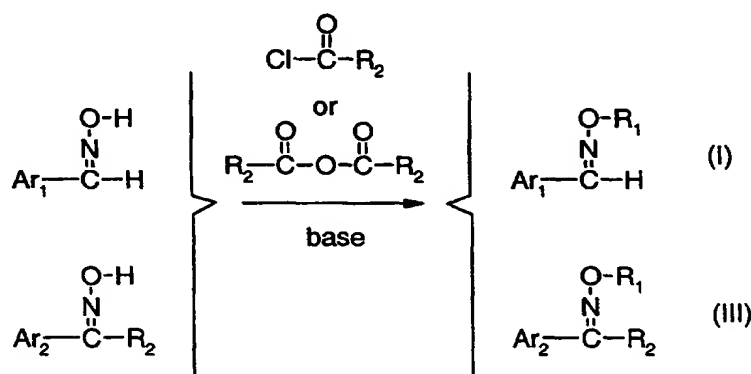
C₃-C₆alkenoyl radicals may be mono- or polyunsaturated and are for example propenoyl, 2-methyl-propenoyl, butenoyl, pentenoyl, 1,3-pentadienoyl, 5-hexenoyl.

Halogen is fluorine, chlorine, bromine and iodine, especially fluorine, chlorine and bromine, preferably fluorine and chlorine.

If the substituents OR₃, SR₄ and NR₅R₆ on a phenyl ring form 5- or 6-membered rings *via* the radicals R₃, R₄, R₅ and/or R₆ with further substituents on the phenyl ring or with one of the carbon atoms of the phenyl ring, structures comprising two or four rings (inclusive the phenyl ring or naphthyl-, anthracyl- or phenanthryl-ring) are obtained. Examples are



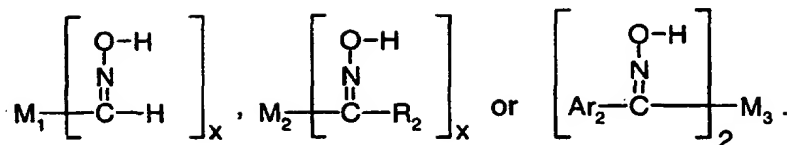
Oxime esters of formulae I, II, III, IV and V are prepared by methods described in the literature, for example by reaction of the corresponding oximes (R₂ = H) with an acyl chloride or an anhydride in an inert solvent such as for example *t*-Butyl methyl ether, tetrahydrofuran (THF) or dimethylformamide (DMF) in the presence of a base, for example triethylamine or pyridine, or in a basic solvent such as pyridine.



Such reactions are well known to those skilled in the art, and are generally carried out at temperatures of -15 to +50°C, preferably 0 to 25°C.

The compounds of formulae II, IV and V can be obtained analogously by using the appropriate oximes as starting materials:

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M_1 - M_3 , R_2 and Ar_2 have the meanings given above.

The oximes required as starting materials can be obtained by a variety of methods described in standard chemistry textbooks (for instance in J. March, *Advanced Organic Chemistry*, 4th Edition, Wiley Interscience, 1992), or in specialized monographs, for example, S.R. Sandler & W. Karo, *Organic functional group preparations*, Vol. 3, Academic Press.

One of the most convenient methods is, for example, the reaction of aldehydes or ketones with hydroxylamine or its salt in polar solvents like ethanol or aqueous ethanol. In that case, a base such as sodium acetate or pyridine is added to control the pH of the reaction mixture. It is well known that the rate of the reaction is pH-dependent, and the base can be added at the beginning or continuously during the reaction. Basic solvents such as pyridine can also be used as base and/or solvent or cosolvent. The reaction temperature is generally the refluxing temperature of the mixture, usually 60-120°C.

Another convenient synthesis of oximes is the nitrosation of "active" methylene groups with nitrous acid or an alkyl nitrite. Both alkaline conditions, as described for example in *Organic Syntheses coll. Vol. VI* (J. Wiley & Sons, New York, 1988), pp 199 and 840, and acidic conditions, as described, for example, in *Organic Synthesis coll. vol V*, pp 32 and 373; *coll. vol. III*, pp 191 and 513, *coll. vol.II*, pp. 202, 204 and 363, are suitable for the preparation of the oximes used as starting materials in the invention. Nitrous acid is usually generated from sodium nitrite. The alkyl nitrite can be for example methyl nitrite, ethyl nitrite, isopropyl nitrite, butyl nitrite, or isoamyl nitrite.

Every oxime ester group can exist in two configurations, (Z) or (E). It is possible to separate the isomers by conventional methods, but it is also possible to use the isomeric mixture as photoinitiating species. Therefore, the invention also relates to mixtures of configurational isomers of compounds of the formulae I, II, III, IV and V.

Especially interesting as photoinitiators for the compositions according to the present invention are compounds of formula I and II.

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Preferred is a photosensitive composition as described above, wherein component (B) is a compound of formula I, wherein

R_1 is C_1 - C_8 alkanoyl;

Ar_1 is C_6 - C_{14} aryl which is unsubstituted or substituted by C_1 - C_4 alkyl, or OR_3 , wherein the substituents OR_3 , optionally form 5- or 6-membered rings *via* the radicals R_3 with further substituents on the aryl ring of the C_6 - C_{20} aryl;

R_3 is C_1 - C_4 alkyl.

Especially interesting as photoinitiators for the compositions according to the present invention are compounds of formula I and II.

Of further interest is a photosensitive composition as described above, wherein component (B) is a compound of formula I, wherein

R_1 is C_1 - C_4 alkanoyl;

Ar_1 is C_6 - C_{14} aryl which is unsubstituted or is substituted 1 to 3 times by halogen, C_1 - C_4 alkyl or OR_3 ; and

R_3 is C_1 - C_4 alkyl.

The compounds of the formulae I, II, III, IV and V can be used as photoinitiators for the photopolymerization of ethylenically unsaturated compounds or of mixtures which comprise such compounds.

Component (A) in the composition according to the invention is an oligomer or polymer, which contains at least one free carboxylic acid group in the molecule.

Examples for suitable components (A) are of binders, such as for example polymers having a molecular weight of about 2'000 to 2'000'000, preferably 5'000 to 1'000'000. Examples of alkali developable binders are acrylic polymer having carboxylic acid function as a pendant group, such as conventionally known copolymers obtained by copolymerizing an ethylenic unsaturated carboxylic acid such as (meth)acrylic acid, 2-carboxyethyl (meth)acrylic acid, 2-carboxypropyl (meth)acrylic acid itaconic acid, crotonic acid, maleic acid and fumaric acid, with one or more monomers selected from esters of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, benzyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, benzyl (meth)acrylate; vinyl aromatic compounds, such as styrene, *a*-methylstyrene, vinyltoluene, *p*-chlorostyrene; amide type unsaturated compounds,

(meth)acrylamide diacetoneacrylamide, N-methylolacrylamide, N-butoxymethacrylamide; and polyolefin type compounds, such as butadiene, isoprene, chloroprene and the like; methacrylonitrile, methyl isopropenyl ketone, vinyl acetate, vinyl propionate, or vinyl pivalate. Examples of copolymers are copolymers of acrylates and methacrylates with acrylic acid or methacrylic acid and with styrene or substituted styrene, phenolic resins, for example novolak, (poly)hydroxystyrene, and copolymers of hydroxystyrene with alkyl acrylates, acrylic acid and/or methacrylic acid. Preferable examples of copolymers are copolymers of methyl methacrylate/methacrylic acid, copolymers of benzyl methacrylate/methacrylic acid, copolymers of methyl methacrylate/ethyl acrylate/methacrylic acid, copolymers of benzyl methacrylate/methacrylic acid/styrene, copolymers of benzyl methacrylate/methacrylic acid/hydroxyethyl methacrylate, copolymers of methyl methacrylate/butyl methacrylate/methacrylic acid/styrene, copolymers of methyl methacrylate/benzyl methacrylate/methacrylic acid/hydroxyphenyl methacrylate.

The polyimide binder resin in the present invention can either be a solvent soluble polyimide or a polymimide precursor, for example a poly(amic acid ester) compound, optionally having photopolymerizable side groups either attached to the backbone or to the ester groups in the molecule, or it can be, for example, a poly(amic acid) to which preferably an acrylate or methacrylate having at least one basic group in its molecule is added in solution, for example an aminoacrylate or aminomethacrylate.

Further examples for component (A) are oligomers or polymers obtained by reaction of a saturated or unsaturated polybasic acid anhydride with a product of the reaction of an epoxy compound and an unsaturated monocarboxylic acid. As epoxy compounds which are employed for the preparation the most interesting ones are novolak type epoxies.

The aforementioned resin curable by an activated energy ray is obtained by causing a reaction product of a novolak type epoxy compound (as described afterward) and an unsaturated monocarboxylic acid to react with a dibasic acid anhydride such as phthalic anhydride or an aromatic polycarboxylic acid anhydride such as trimellitic acid anhydride or pyromellitic acid anhydride. In this case, the resin proves particularly suitable when, in the production thereof, the amount of the aforementioned acid anhydride used for the reaction exceeded 0.15 mol per each of the hydroxyl groups possessed by the reaction product of the novolak type epoxy compound and the unsaturated carboxylic acid.

The acid value of the resin so obtained suitably falls in the range of 45 to 160 mg KOH/g, preferably 50 to 140 mg KOH/g.

When the number of ethylenically unsaturated bonds present in the molecular unit of the resin curable by the activated energy ray is small, the photosetting proceeds slowly and it is desirable to use a novolak type epoxy compound as a raw material. For the purpose of lowering the viscosity of the ink, it is possible to use bis-phenol A type epoxy compounds instead.

The novolak type epoxy compounds are represented by phenol novolak type epoxy resins and cresol novolak type epoxy resins. Compounds as are produced by causing epichlorohydrin to react with a pertinent novolak resin by the conventional method can be used.

Typical examples of the aforementioned acid anhydride are dibasic acid anhydrides such as for example maleic anhydride, succinic anhydride, itaconic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, methyhexahydrophthalic anhydride, endomethylenetetrahydrophthalic anhydride, methyl-dneomethylenetetrahydrophthalic anhydride, chlorendic anhydride, and methyltetrahydrophthalic anhydride; aromatic polycarboxylic anhydrides such as for example trimellitic anhydride pyromellitic anhydride, and benzophenone-tetracarboxylic dianhydride; and polycarboxylic anhydride derivatives such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride.

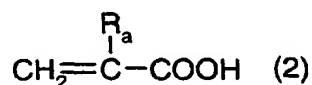
Further examples for component (A) are reaction products obtained by adding epoxy group containing acrylic acid ester or methacrylic acid ester compounds to a part of the carboxyl groups of a copolymer resulting of the reaction of acrylate or methacrylate with acrylic acid or methacrylic acid.

The copolymer of acrylic acid ester and/or methacrylic acid ester and acrylic acid and/or methacrylic acid is obtained by copolymerizing one or two or more of acrylic acid esters and/or methacrylic acids represented by the general formula (1) and (2)



R_a is a hydrogen atom or a methyl group, R_b is an aliphatic hydrocarbon group having 1 to 6 carbon atoms,

and acrylic acid and/or methacrylic acid represented by the general formula (2);



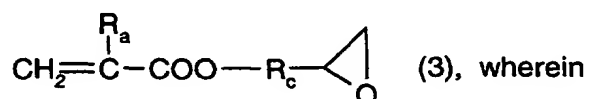
wherein R_a has the same meaning as given above, according to routine methods such as solution polymerization.

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Preferably the molar ratio between the acrylic acid ester and/or methacrylic acid ester and the acrylic acid and/or methacrylic acid is from 30:70 to 70:30.

The ester group of each of the acrylic acid ester and/or methacrylic acid ester may be appropriately selected from various aliphatic groups containing 1 to 6 carbon atoms.

The reaction product is obtained by adding to the copolymer thus obtained acrylic acid ester and/or methacrylic acid ester having a terminal epoxy group, represented by the following general formula (3);



R_a has the same meaning as described above;

R_c is an aliphatic hydrocarbon group or aromatic hydrocarbon group having 1 to 12 carbon atoms.

In order to obtain the reaction product suitable for the present invention, a compound of formula (3) is added to the aforementioned monomers of formula (1) and (2) at a ratio of 10 to 40 mol %, to provide the copolymer with ultraviolet curability.

The reaction product thus obtained is preferably has an average molecular weight in the range of 20'000 to 70'000; the softening point suitably is in the range from 35°C to 130°C, and the acid value is 50 to 150.

Further examples for component (A) are resins having α,β -unsaturated double bonds on the side chains, and having an acid value of 50-200. The photopolymerizable resin, for example, is constituted of 70-95% by weight of an ethylenically unsaturated acid component and a copolymerizable component thereof. It is an addition product formed between a carboxyl group-containing resin having an acid value (the acid value is expressed by milligram number of potassium hydroxide necessary for neutralizing 1 gram of resin) of no less than 500, preferably no less than 600 and in particular no less than 620, and having a number average molecular weight of 1'000-100'000, preferably 3'000-70'000, and an unsaturated compound having an α,β -unsaturated double bond and an epoxy group. The content of the ethylenically unsaturated acid component in the carboxyl group-containing resin of the photopolymerizable resin is 70-95% by weight, due to which the photopolymerizable resin (A) does not become insoluble in water or dilute alkaline aqueous solution even after an unsaturated compound having an α,β -unsaturated double bond and an epoxy group is added thereto, and retains its solubility. Examples of such resins are described in JP 8-339081-A.

The carboxyl group-containing resin (A), for example, is produced by dissolving 70-95% by weight, preferably 78-88% by weight and in particular 80-85% by weight, of an ethylenically unsaturated acid monomer and 5-30% by weight, preferably 22-12% by weight and in particular 15-20% by weight, of a copolymerizable monomer in a suitable unreactive solvent and thermally polymerizing the solution at 45-120°C in the presence of a thermal polymerization initiator. Thus, a carboxyl group-containing resin having an acid value of no less than 500 and a number average molecular weight of 1'000-100'000 can be produced in a high safety and a high stability.

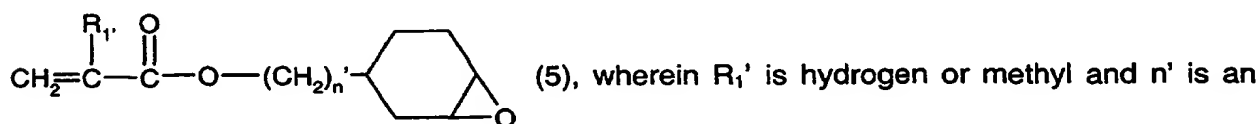
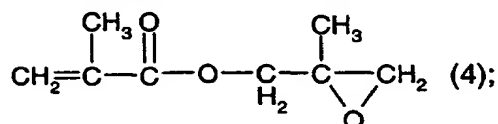
Specific examples of the ethylenically unsaturated monomer suitable for production of the carboxyl group-containing resin (A) include acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, succinic acid mono-hydroxyethylacrylate, phthalic acid mono-hydroxyethylacrylate, dihydrophthalic acid mono-hydroxyethylacrylate, tetrahydrophthalic acid mono-hydroxyethylacrylate, hexahydrophthalic acid monohydroxyethyl-acrylate, acrylic acid dimer, acrylic acid trimer, ω -carboxy-polycaprolactone monoacrylate and ω -carboxy-polycaprolactone monomethacrylate. Among these monomers, preferred are acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, ω -carboxy-polycaprolactone monoacrylate, ω -carboxy-polycaprolactone monomethacrylate, and the like; and particularly preferred are acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, angelic acid, tiglic acid, 2-ethylacrylic acid, 3-propylacrylic acid, 3-isopropylacrylic acid, ω -carboxy-polycaprolactone monoacrylate, and ω -carboxy-polycaprolactone monomethacrylate. These monomers may be used either alone or in mixture of two or more.

Suitable copolymerizable monomers are acrylic esters, methacrylic esters, vinyl monomers, styrene type monomers and cyclic ester monomers. Specific examples thereof include 2-hydroxymethyl acrylate, 2-hydroxymethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, ethyleneglycol monomethyl ether acrylate, ethyleneglycol monomethyl ether methacrylate, ethyleneglycol monoethyl ether acrylate, ethyleneglycol monoethyl ether methacrylate, glycerol acrylate, glycerol methacrylate, dipentaerythritol pentamethacrylate, dipentaerythritol pentaacrylate, dimethylaminoethyl acrylate, dimethylamino-ethyl methacrylate, tetrahydrofurfuryl acrylate, tetrahydro-furfuryl methacrylate, acrylic acid amide, methacrylic acid amide, acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, isobutyl acrylate, isobutyl methacrylate, 2-ethylhexyl acrylate, 2-

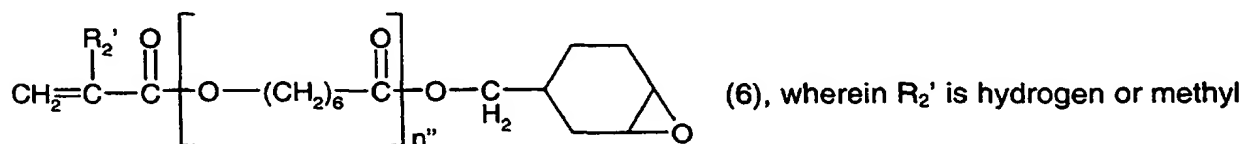
ethylhexyl-methacrylate, benzyl acrylate, benzyl methacrylate, acrylic acid carbitol, methacrylic acid carbitol, ϵ -caprolactone-modified tetrafurfuryl acrylate, ϵ -caprolactone-modified tetrafurfuryl methacrylate, diethyleneglycol ethoxyl acrylate, isodecyl acrylate, isodecyl methacrylate, octyl acrylate, octyl methacrylate, lauryl acrylate, lauryl methacrylate, tridecyl acrylate, tridecyl methacrylate, stearyl acrylate, stearyl methacrylate and the like. These monomers may be used either alone or in mixtures of two or more.

Suitable thermal polymerization initiators are for example, 2,2'-azobis-(2,4-dimethylvaleronitrile) (usable temperature 45-70°C), 2,2'-azobis(isobutyronitrile) (usable temperature 60-90°C), 2,2'-azobis(2-methylisobutyronitrile) (usable temperature 60-95°C), tert-butyl peroctoate (usable temperature 75-100°C), 1,1'-azobis(cyclohexane-1-carbonitrile) (usable temperature 80-110°C) or 1-[(1-diazo-1-methylethyl)azo]-formamide (usable temperature 95-120°C). At least one of the cited compounds is used.

The carboxyl group-containing resin produced according to the aforementioned method is then modified into a photopolymerizable resin whose carboxyl group is esterified and whose side chains have α,β -unsaturated double bonds, through an esterification with an unsaturated compound having an α,β -unsaturated double bond and a epoxy group. Examples of suitable compounds having an α,β -unsaturated double bond and an epoxy group, are given below. At least one member selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, compounds of the formula 4, 5, 6, as defined below, is used.



integer of 1-10;



and n'' is an integer of 1-3.

Among these compounds, compounds having alicyclic epoxy groups are particularly preferred, because these compounds have a high reactivity with carboxyl group-containing resins, accordingly the reaction time can be shortened. These compounds further do not cause gela-

tion in the process of reaction and make it possible to carry out the reaction stably. On the other hand, glycidyl acrylate and glycidyl methacrylate are advantageous from the viewpoint of sensitivity and heat resistance because they have a low molecular weight and can give a high conversion of esterification.

The photopolymerizable resin obtained by the above-mentioned method has α,β -unsaturated double bonds on its side chains. Its acid value is 50-200, preferably 70-150, and in particular 85-120. Its number average molecular weight is 7'000-10'000, and its glass transition point (hereinafter referred to as Tg) is 30-120°C. When the photopolymerizable resin is used as a solder resist, an acid value of no less than 70 is preferable, because other additive ingredients may further be added to the composition.

An inert organic solvent is used at the time of carrying out the esterification and preparing the photosensitive resin composition.

Commercially available unsaturated compounds (A), as described before are, for example EB3800, EB9692, EB9694, EB9695, EB9696 (UCB Chemicals), KAYARAD TCR1025 (Nippon Kayaku Co.,LTD.), NEOPOL8319 (U-Pica), EA-6340 (Shin Nakamura Chemical Co., Ltd.), ACA200M, ACA250 (Daicel Industries, Ltd.).

Preferred is a composition, wherein the oligomer or polymer (A) is a binder polymer, in particular a copolymer of (meth)acrylate and (meth)acrylic acid, or a resin obtained by the reaction of a saturated or unsaturated polybasic acid anhydride with a product of the reaction of an epoxy compound and an unsaturated monocarboxylic acid, or is an addition product formed between a carboxyl group-containing resin and an unsaturated compound having an α,β -unsaturated double bond and an epoxy group.

Subject of the invention also is a photosensitive composition as described above additionally comprising an epoxy compound which contains at least two epoxy groups in the molecule as a thermosetting component.

Examples of reactive or unreactive diluents (C) which are suitable in the compositions according to the invention are photopolymerizable vinyl type monomers and/or an organic solvents. Representative examples of the photopolymerizable vinyl type monomers are hydroxyalkyl acrylates such as 2-hydroxyethyl acrylate, 2-hydroxybutyl acrylate, etc.; mono- or diacrylates of glycols such as ethylene glycol, methoxytetraethylene glycol, polyethylene glycol,

propylene glycol, etc.; acrylamides such as N,N-dimethylacrylamide, N-methylolacrylamide, etc.; aminoalkyl acrylates such as N,N-dimethylaminoethyl acrylate, etc.; polyvalent acrylates of polyvalent alcohols or ethylene oxide or propylene oxide adducts thereof such as hexanediol, trimethylolpropane, pentaerythritol, dipentaerythritol, tris-hydroxyethyl isocyanurate, etc.; phenoxy acrylate, bisphenol A diacrylate and acrylates of ethylene oxide or propylene oxide adducts of these phenols, etc.; acrylates of glycidyl ethers such as glycerin diglycidyl ether, trimethylolpropane triglycidyl ether, triglycidyl isocyanurate, etc.; and melamine acrylate, and/or methacrylates corresponding to the above acrylates, etc.

On the other hand, examples for suitable organic solvents are ketones such as ethyl methyl ketone, cyclohexanone, etc.; aromatic hydrocarbons such as toluene, xylene, tetramethylbenzene, etc.; glycol ethers such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, benzyl cellosolve, phenyl cellosolve, methylcarbitol, butylcarbitol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monobutyl ether, triethylene glycol monoethyl ether, etc.; esters such as ethyl acetate, butyl acetate and esterified products of the above glycol ethers such as cellosolve acetate, butyl cellosolve acetate, carbitol acetate, butyl carbitol acetate; alcohols such as ethanol, propanol, n-butanol, n-hexanol, n-heptanol, n-octanol, ethylene glycol, propylene glycol, etc.; aliphatic hydrocarbons such as octane, decane, etc.; a petroleum type solvent such as petroleum ether, petroleum naphtha, hydrogenated petroleum naphtha, solvent naphtha, etc. and others. The organic solvent is used for diluting the resin so that it can be coated easily.

The diluents (C) as described above are used singly or as a mixture of two or more of them. The suitable amount is from 5 to 300 parts by weight, preferably 10 to 150 parts by weight, based on 100 parts by weight of component (A).

The above described diluent is used to dilute the components of the mixture so that they can be coated easily. Another purpose, if a photopolymerizable vinyl type monomer is used, is to strengthen the photopolymerizability. Further, if an organic solvent is used as diluent, the diluent supports to dissolve and dilute the photosensitive prepolymer, whereby the prepolymer can be coated in a liquid state and then dried to form a film. Therefore, depending on the diluent used, an exposure system of either a contact system in which a photomask is contacted with the coating film or a non-contact system (e.g. laser beam writing) may be used.

Preferably component (C) is a monomer with more than two acrylate or methacrylate groups.

Photopolymerization can also be accelerated by adding further photosensitizers or coinitiators (as component (D)) which shift or broaden the spectral sensitivity. These are, in particular, aromatic compounds, for example benzophenone and derivatives thereof, thioxanthone and derivatives thereof, anthraquinone and derivatives thereof, coumarin and phenothiazine and derivatives thereof, and also 3-(aroylmethylene)thiazolines, rhodanine, camphorquinone, but also eosine, rhodamine, erythrosine, xanthene, thioxanthene, acridine, e.g. 9-phenylacridine, 1,7-bis(9-acridinyl)heptane, 1,5-bis(9-acridinyl)pentane, cyanine and merocyanine dyes.

Specific examples of such compounds are

1. Thioxanthenes

Thioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-dodecylthioxanthone, 2,4-diethylthioxanthone, 2,4-dimethylthioxanthone, 1-methoxycarbonylthioxanthone, 2-ethoxycarbonylthioxanthone, 3-(2-methoxyethoxycarbonyl)-thioxanthone, 4-butoxycarbonylthioxanthone, 3-butoxycarbonyl-7-methylthioxanthone, 1-cyano-3-chlorothioxanthone, 1-ethoxycarbonyl-3-chlorothioxanthone, 1-ethoxycarbonyl-3-ethoxythioxanthone, 1-ethoxycarbonyl-3-aminothioxanthone, 1-ethoxycarbonyl-3-phenylsulfurylthioxanthone, 3,4-di-[2-(2-methoxyethoxy)-ethoxycarbonyl]-thioxanthone, 1-ethoxycarbonyl-3-(1-methyl-1-morpholinoethyl)-thioxanthone, 2-methyl-6-dimethoxymethyl-thioxanthone, 2-methyl-6-(1,1-dimethoxybenzyl)-thioxanthone, 2-morpholinomethylthioxanthone, 2-methyl-6-morpholinomethylthioxanthone, N-allylthioxanthone-3,4-dicarboximide, N-octylthioxanthone-3,4-dicarboximide, N-(1,1,3,3-tetramethylbutyl)-thioxanthone-3,4-dicarboximide, 1-phenoxythioxanthone, 6-ethoxycarbonyl-2-methoxythioxanthone, 6-ethoxycarbonyl-2-methylthioxanthone, thioxanthone-2-carboxylic acid polyethyleneglycol ester, 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthone-2-yloxy)-N,N,N-trimethyl-1-propanaminium chloride;

2. Benzophenones

benzophenone, 4-phenyl benzophenone, 4-methoxy benzophenone, 4,4'-dimethoxy benzophenone, 4,4'-dimethyl benzophenone, 4,4'-dichlorobenzophenone 4,4'-bis(dimethylamino)-benzophenone, 4,4'-bis(diethylamino)benzophenone, 4-methyl benzophenone, 2,4,6-trimethylbenzophenone, 4-(4-methylthiophenyl)-benzophenone, 3,3'-dimethyl-4-methoxy benzophenone, methyl-2-benzoylbenzoate, 4-(2-hydroxyethylthio)-benzophenone, 4-(4-tolylthio)-benzophenone, 4-benzoyl-N,N,N-trimethylbenzenemethanaminium chloride, 2-hydroxy-3-(4-benzoylphenoxy)-N,N,N-trimethyl-1-propanaminium chloride monohydrate, 4-(13-acryloyl-

1,4,7,10,13-pentaoxatridecyl)-benzophenone, 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oxy]ethyl-benzenemethanaminium chloride;

3. Coumarins

Coumarin 1, Coumarin 2, Coumarin 6, Coumarin 7, Coumarin 30, Coumarin 102, Coumarin 106, Coumarin 138, Coumarin 152, Coumarin 153, Coumarin 307, Coumarin 314, Coumarin 314T, Coumarin 334, Coumarin 337, Coumarin 500, 3-benzoyl coumarin, 3-benzoyl-7-methoxycoumarin, 3-benzoyl-5,7-dimethoxycoumarin, 3-benzoyl-5,7-dipropoxycoumarin, 3-benzoyl-6,8-dichlorocoumarin, 3-benzoyl-6-chloro-coumarin, 3,3'-carbonyl-bis[5,7-di(propoxy)-coumarin], 3,3'-carbonyl-bis(7-methoxycoumarin), 3,3'-carbonyl-bis(7-diethylamino-coumarin), 3-isobutyroylcoumarin, 3-benzoyl-5,7-dimethoxy-coumarin, 3-benzoyl-5,7-diethoxy-coumarin, 3-benzoyl-5,7-dibutoxycoumarin, 3-benzoyl-5,7-di(methoxyethoxy)-coumarin, 3-benzoyl-5,7-di(allyloxy)coumarin, 3-benzoyl-7-dimethylaminocoumarin, 3-benzoyl-7-diethylaminocoumarin, 3-isobutyroyl-7-dimethylaminocoumarin, 5,7-dimethoxy-3-(1-naphthoyl)-coumarin, 5,7-diethoxy-3-(1-naphthoyl)-coumarin, 3-benzoylbenzo[f]coumarin, 7-diethylamino-3-thienoylcoumarin, 3-(4-cyanobenzoyl)-5,7-dimethoxycoumarin, 3-(4-cyanobenzoyl)-5,7-dipropoxycoumarin, 7-dimethylamino-3-phenylcoumarin, 7-diethylamino-3-phenylcoumarin, the coumarin derivatives disclosed in JP 09-179299-A and JP 09-325209-A, for example 7-[(4-chloro-6-(diethylamino)-S-triazine-2-yl)amino]-3-phenylcoumarin;

4. 3-(aroylmethylene)-thiazolines

3-methyl-2-benzoylmethylene- β -naphthothiazoline, 3-methyl-2-benzoylmethylene-benzothiazoline, 3-ethyl-2-propionylmethylene- β -naphthothiazoline;

5. Rhodanines

4-dimethylaminobenzalrhodanine, 4-diethylaminobenzalrhodanine, 3-ethyl-5-(3-octyl-2-benzothiazolinyldiene)-rhodanine, the rhodanine derivatives, formulae [1], [2], [7], disclosed in JP 08-305019A;

6. Other compounds

acetophenone, 3-methoxyacetophenone, 4-phenylacetophenone, benzil, 4,4'-bis(dimethylamino)benzil, 2-acetylnaphthalene, 2-naphthaldehyde, dansyl acid derivatives, 9,10-anthraquinone, anthracene, pyrene, aminopyrene, perylene, phenanthrene, phenanthrenequinone, 9-fluorenone, dibenzosuberone, curcumin, xanthone, thiomichler's ketone, α -(4-dimethylaminobenzylidene) ketones, e.g. 2,5-bis(4-diethylaminobenzylidene)cyclopentanone, 2-(4-dimethylamino-benzylidene)-indan-1-one, 3-(4-dimethylamino-phenyl)-1-indan-5-yl-propenone, 3-phenylthiophthalimide, N-methyl-3,5-di(ethylthio)-phthalimide, N-methyl-3,5-di(ethylthio)-phthalimide, phenothiazine, methylphenothiazine, amines, e.g. N-phenylglycine, ethyl 4-di-

methylaminobenzoate, butoxyethyl 4-dimethylaminobenzoate, 4-dimethylaminoacetophenone, triethanolamine, methyldiethanolamine, dimethylaminoethanol, 2-(dimethylamino)ethyl benzoate.

A photopolymerizable composition, comprising as further additive (D) a photosensitizer compound selected from the group consisting of benzophenone and its derivatives, thioxanthone and its derivatives, anthraquinone and its derivatives, or coumarin derivatives is preferred.

Component (D) is suitably used in an amount from 0.015 to 60 parts by weight, preferably 0.03 to 30 parts by weight, based on 100 parts by weight of component (A).

In some cases it may be advantageous to use sensitizer compounds in combination with the compounds of the formula I, II, III, IV and V. Another object of the invention therefore resides in a composition which additionally to the components (A), (B) and (C) comprises at least one photosensitizer compound (D), and/or further additives (E).

In addition to the photoinitiator and/or the sensitizer compound the photopolymerizable mixtures may include various additives (E).

Examples of these are compounds having epoxy groups as thermosetting component. There may be used a solid or liquid known epoxy compound, and said epoxy compound is used depending on required characteristics. For example, when the plating resistance is to be improved, a liquid epoxy resin is used, and when water resistance is required, an epoxy resin having a large number of methyl groups on a benzene ring or a cycloalkyl ring is employed. A preferred epoxy resin, is a bisphenol S type epoxy resin such as BPS-200 produced by Nippon Kayaku Co., Ltd., EPX-30 produced by ACR Co., Epiculon EXA-1514 produced by Dainippon Ink & Chemicals Inc., etc.; a bisphenol A type epoxy resin such as Epiculon N-3050, N-7050, N-9050 produced by Dainippon Ink & Chemicals Inc., XAC-5005, GT-7004, 6484T, 6099 produced by Ciba Specialty Chemicals Inc., etc. ; a bisphenol F type epoxy resin such as YDF-2004, YDF2007 produced by Tohto Kasei Co., etc. ; a diglycidyl phthalate resin such as Blemmer DGT produced by Nippon Oil and Fats Co., Ltd., etc.; a heterocyclic epoxy resin such as TEPIC produced by Nissan Chemical Industries, Ltd., Araldite PT810 produced by Ciba Specialty Chemicals Inc., etc.; a bixylenol type epoxy resin such as YX-4000 produced by Yuka Shell Co., etc.; a biphenol type epoxy resin such as YL-6056 produced by Yuka Shell Co., etc.; a tetraglycidyl xylenoylethane resin such as ZX-1063

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produced by Tohto Kasei Co., etc.; a novolak type epoxy resin such as EPPN-201, EOCN-103, EOCN-1020, EOCN-1025 and BRRN produced by Nippon Kayaku Co., Ltd., ECN-278, ECN-292 and ECN-299 produced by Asahi Chemical Industry Co., Ltd., GY-1180, ECN-1273 and ECN-1299 produced by Ciba Specialty Chemicals Inc., YDCN-220L, YDCN-220HH, YDCN-702, YDCN-704, YDPN-601 and YDPN-602 produced by Tohto Kasei Co., Epiculon-673, N-680, N-695, N-770 and N-775 produced by Dainippon Ink & Chemicals Inc., etc.; a novolak type epoxy resin of bisphenol A such as EPX-8001, EPX-8002, EPPX-8060 and EPPX-8061 produced by Asahi Chemical Industry Co., Ltd., Epiculon N-880 produced by Dainippon Ink & Chemicals Inc., etc.; a chelate type epoxy resin such as EPX-49-69 and EPX-49-30 produced by Asahi Denka Kogyo K.K., etc.; a glyoxal type epoxy resin such as YDG-414 produced by Tohto Kasei Co., etc.; an amino group-containing epoxy resin such as YH-1402 and ST-110 produced by Tohto Kasei Co., YL-931 and YL-933 produced by Yuka Shell Co., etc.; a rubber-modified epoxy resin such as Epiculon TSR-601 produced by Dainippon Ink & Chemicals Inc., EPX-84-2 and EPX-4061 produced by Asahi Denka Kogyo K.K., etc.; a dicyclopentadiene phenolic type epoxy resin such as DCE-400 produced by Sanyo-Kokusaku Pulp Co., Ltd., etc.; a silicone-modified epoxy resin such as X-1359 produced by Asahi Denka Kogyo K.K., etc.; an e-caprolactone-modified epoxy resin such as Plaque G-402 and G-710 produced by Dical Chemical Industries, Ltd., etc. and others. Further, partially esterified compounds of these epoxy compounds (e.g. esterified by (meth)acrylates) can be used in combination.

The suitable amount of thermosetting component to be used according to the present invention is 10 to 150 parts by weight, preferably 20 to 80 parts by weight, based on 100 parts by weight of component (A).

Preferably thermosetting component is a bisphenol A, bisphenol S, bisphenol F or novolak type epoxy compound.

Examples of further additives (E) are thermal inhibitors, which are intended to prevent premature polymerization, examples being hydroquinone, hydroquinone derivatives, p-methoxyphenol, β -naphthol or sterically hindered phenols, such as 2,6-di-tert-butyl-p-cresol. In order to increase the stability on storage in the dark it is possible, for example, to use copper compounds, such as copper naphthenate, stearate or octoate, phosphorus compounds, for example triphenylphosphine, tributylphosphine, triethyl phosphite, triphenyl phosphite or tribenzyl phosphite, quaternary ammonium compounds, for example tetra-

methyammonium chloride or trimethylbenzylammonium chloride, or hydroxylamine derivatives, for example N-diethylhydroxylamine. To exclude atmospheric oxygen during the polymerization it is possible to add paraffin or similar wax-like substances which, being of inadequate solubility in the polymer, migrate to the surface in the beginning of polymerization and form a transparent surface layer which prevents the ingress of air. It is also possible to apply an oxygen-impermeable layer. Light stabilizers which can be added in a small quantity are UV absorbers, for example those of the hydroxyphenylbenzotriazole, hydroxyphenyl-benzophenone, oxalamide or hydroxyphenyl-s-triazine type. These compounds can be used individually or in mixtures, with or without sterically hindered amines (HALS).

Examples of such UV absorbers and light stabilizers are

1. 2-(2'-hydroxyphenyl)benzotriazoles for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethyl-hexyl-oxy)carbonyl]ethyl)-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)-benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonyl)ethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-yl-phenol]; transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl)ethyl)-2'-hydroxyphenyl)-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_2-$ where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-yl-phenyl.

2. 2-Hydroxybenzophenones, for example the 4-hydroxy-, 4-methoxy-, 4-octoxy-, 4-decyloxy-, 4-dodecyloxy-, 4-benzyloxy-, 4,2',4'-trihydroxy- and 2'-hydroxy-4,4'-dimethoxy derivative.

3. Esters of substituted or unsubstituted benzoicacids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, and 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

4. Acrylates, for example isooctyl or ethyl α -cyano- β , β -diphenyl acrylate, methyl α -carboxymethoxycinnamate, butyl or methyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carboxymethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

5. Sterically hindered amines, for example bis-(2,2,6,6-tetramethylpiperidyl) sebacate, bis-(2,2,6,6-tetramethylpiperidyl) succinate, bis-(1,2,2,6,6-pentamethylpiperidyl) sebacate, bis-(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, condensation product of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexa-methylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris-(2,2,6,6-tetramethyl-4-piperidyl) nitri-lotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetraoate, 1,1'-(1,2-ethandiyl)bis(3,3,5,5-tetramethyl-piperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis-(1,2,2,6,6-pentamethylpiperidyl) 2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis-(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis-(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, condensation product of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, condensation product of 2-chloro-4,6-di-(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropyl-amino)ethane, condensation product of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)-ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione; 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione and 3-dodecyl-1-(1,2,2,6,6-penta-methyl-4-piperidyl)-pyrrolidine-2,5-dione.

6. Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis-(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide, mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanalides.

7. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxy-phenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-

bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-dodecyl/tridecyl-oxy-(2-hydroxypropyl)oxy-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

8. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythrityl diphosphite, tris-(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythrityl diphosphite, bis-(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, bis-(2,6-di-tert-butyl-4-methylphenyl) pentaerythrityl diphosphite, bis-isodecyloxy pentaerythrityl diphosphite, bis-(2,4-di-tert-butyl-6-methylphenyl) pentaerythrityl diphosphite, bis-(2,4,6-tri-tert-butylphenyl) pentaerythrityl diphosphite, tristearyl sorbityl triphosphite, tetrakis-(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-di-benzo[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocine, bis-(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite.

In the photosensitive thermosetting resin composition of the present invention, for improving characteristics such as adhesion property, hardness, etc., if necessary, there may be used an inorganic filler such as for example barium sulfate, barium titanate, silicon oxide powder, particulate silicone oxide, amorphous silica, talc, clay, magnesium carbonate, calcium carbonate, aluminium oxide, aluminium hydroxide, mica powder, etc. The ration of the filler in the formulation is 0 to 60 % by weight, preferably 5 to 40 % by weight of the photosensitive thermosetting resin composition.

Further, if, necessary, there may be used known additives such as a known coloring agents, e.g. Phthalocynine Blue, Phthalocyanine Green, Diazo Yellow, Crystal Violet, titanium oxide, carbone black, naphthalene black, etc..

The composition optionally additionally comprises as component (E) epoxy curing promoters such as, for example, an amine compound, an imidazole compound, a carboxylic acid, a phenol, a quaternary ammonium salt, or a methylol group-containing compound. The amount of said curing agent to be used is in the range of 0 to 10 % by weight, preferably 0.05 to 5 % by weight, of the photosensitive thermosetting resin composition.

Accordingly, subject of the invention are compositions as described above, comprising further additives (E), which are selected from the group consisting of inorganic fillers, colour-

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ants, epoxy curing agents, thermal polymerization inhibitors, thickeners, antifoaming agents and leveling agents, in particular inorganic fillers.

To accelerate the photopolymerization it is possible to add amines, for example triethanolamine, N-methyldiethanolamine, p-dimethylaminobenzoate or Michler's ketone. The action of the amines can be intensified by the addition of aromatic ketones of the benzophenone type. Examples of amines which can be used as oxygen scavengers are substituted N,N-dialkylanilines, as are described in EP 339841. Other accelerators, coinitiators and autoxidizers are thiols, thioethers, disulfides, phosphonium salts, phosphine oxides or phosphines, as described, for example, in EP 438123, in GB 2180358 and in JP Kokai Hei 6-68309.

It is further possible to add chain transfer agents which are customary in the art to the compositions according to the invention. Examples are mercaptans, amines and benzothiazol.

The curing process can be assisted by, in particular, compositions which are pigmented (for example with titanium dioxide), and also by adding a component which under thermal conditions forms free radicals, for example an azo compound such as 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), a triazene, diazo sulfide, pentazadiene or a peroxy compound, for instance a hydroperoxide or peroxy carbonate, for example t-butyl hydroperoxide, as described for example in EP 245639.

The compositions according to the invention may comprise as further additive (E) a photoreducible dye, e.g., xanthene-, benzoxanthene-, benzothioxanthene, thiazine-, pyronine-, porphyrine- or acridine dyes, and/or trihalogenmethyl compounds which can be cleaved by irradiation. Similar compositions are for example described in EP 445624.

Further customary additives (E), depending on the intended use, are optical brighteners, wetting agents or levelling assistants.

In order to cure thick and pigmented coatings it is appropriate to add glass microspheres or pulverized glass fibres, as described for example in US 5013768.

The choice of additive(s) (E) is made depending on the field of application and on properties required for this field. The additives described above are customary in the art and accordingly are added in amounts which are usual in the respective application.

In certain cases it may be of advantage to use mixtures of two or more of the photo-initiators according to the invention. It is of course also possible to use mixtures with known photoinitiators (B1), for example mixtures with camphor quinone, benzophenone, benzophenone derivatives, acetophenone, acetophenone derivatives, for example α -hydroxycycloalkyl phenyl ketones or 2-hydroxy-2-methyl-1-phenyl-propanone, dialkoxyacetophenones, α -hydroxy- or α -aminoacetophenones, e.g. (4-methylthiobenzoyl)-1-methyl-1-morpholinoethane, (4-morpholinobenzoyl)-1-benzyl-1-dimethylaminopropane, 4-aryloxy-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, e.g. dimethyl benzil ketal, phenylglyoxalic esters and derivatives thereof, dimeric phenylglyoxalic esters, monoacyl phosphine oxides, e.g. (2,4,6-trimethylbenzoyl)di-phenylphosphine oxide, bisacylphosphine oxides, bis(2,6-dimethoxy-benzoyl)-(2,4,4-trimethyl-pentyl)phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,4,6-trimethylbenzoyl)-2,4-dipentoxyphenylphosphine oxide, trisacylphosphine oxides, ferrocenium compounds, or titanocenes, e.g. bis(cyclopentadienyl)-bis(2,6-difluoro-3-pyrryl-phenyl)titanium.

Where the oxime photoinitiators are employed in hybrid systems, use may be made, in addition to the free-radical hardeners, of cationic photoinitiators, for example peroxide compounds, such as benzoyl peroxide (other suitable peroxides are described in US Patent 4950581 column 19, lines 17-25), aromatic sulfonium-, phosphonium- or iodonium salts as described for example in US Patent 4950581, column 18, line 60 to column 19, line 10 or cyclopentadienyl-arene-iron(II) complex salts, for example (η^6 -iso-propylbenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate, as well as oxime sulfonic acid esters, as are, for example described in EP 780729.

Subject of the invention therefore also is a composition comprising additionally at least one photoinitiator (B1).

In certain cases it may be of advantage to use mixtures of two or more of the novel photoinitiators. It is of course also possible to use mixtures with known photoinitiators (B1), for example mixtures with camphor quinone, benzophenone, benzophenone derivatives, acetophenone, acetophenone derivatives, for example α -hydroxycycloalkyl phenyl ketones or 2-hydroxy-2-methyl-1-phenyl-propanone, dialkoxyacetophenones, α -hydroxy- or α -aminoacetophen-

ones, e.g. (4-methylthiobenzoyl)-1-methyl-1-morpholinoethane, (4-morpholinobenzoyl)-1-benzyl-1-dimethylaminopropane, 4-aryloxy-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, e.g. dimethyl benzil ketal, phenylglyoxalic esters and derivatives thereof, dimeric phenylglyoxalic esters, diacetyl, peresters, e.g. benzophenone tetracarboxylic peresters as described for example in EP 126541, monoacyl phosphine oxides, e.g. (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, bisacylphosphine oxides, bis(2,6-dimethoxy-benzoyl)-(2,4,4-trimethyl-pentyl)phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,4,6-trimethylbenzoyl)-2,4-dipentoxypheylphosphine oxide, trisacylphosphine oxides, halomethyltriazines, e.g. 2-[2-(4-methoxy-phenyl)-vinyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-(4-methoxy-phenyl)-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-(3,4-dimethoxy-phenyl)-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-methyl-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-(4-N,N-di(ethoxycarbonylmethyl)aminophenyl)-4,6-bis(trichloromethyl)-[1,3,5]triazine, 2-(4-methoxynaphthyl)-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-(1,3-benzodioxol-5-yl)-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-[4-(pentyloxy)phenyl]ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-(3-methyl-2-furanyl)-ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-(5-methyl-2-furanyl)-ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-(2,4-dimethoxy-phenyl)-ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-(2-methoxy-phenyl)ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-[4-isopropoxy-phenyl]-ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-(3-chloro-4-methoxy-phenyl)ethenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-bromo-4-N,N-di(ethoxycarbonylmethyl)amino-phenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[2-chloro-4-N,N-di(ethoxycarbonylmethyl)amino-phenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[3-bromo-4-N,N-di(ethoxycarbonylmethyl)amino-phenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, 2-[3-chloro-4-N,N-di(ethoxycarbonylmethyl)amino-phenyl]-4,6-bis-trichloromethyl-[1,3,5]triazine, or other halomethyl-triazines as described for example in G.Buhr, R. Dammel and C. Lindley Polym. Mater. Sci. Eng. 61,269 (1989), and EP 0262788; halomethyl-oxazol photoinitiators, such as described in US 4371606 and US 4371607; 1,2-disulfones, such as described in E. A. Bartmann, Synthesis 5, 490 (1993); hexaaryl-bisimidazole, and hexaaryl-bisimidazole / coinitiators systems, e.g. ortho-chlorohexaphenyl-bisimidazole combined with 2-mercaptobenzthiazole, ferrocenium compounds, or titanocenes, e.g. bis(cyclopentadienyl)-bis(2,6-difluoro-3-pyrryl-phenyl)titanium.

Where the novel photoinitiator systems are employed in hybrid systems, use is made, in addition to the novel free-radical hardeners, of cationic photoinitiators, of peroxide compounds, such as benzoyl peroxide (other suitable peroxides are described in US Patent 4950581 column 19, lines 17-25), of aromatic sulfonium-, phosphonium- or iodonium salts as described for example in US Patent 4950581, column 18, line 60 to column 19, line 10 or cyclopenta-

dienyl-arene-iron(II) complex salts, for example (η^6 -iso-propylbenzene)(η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate, as well as oxime sulfonic acid esters, as are, for example described in EP 780729. Also pyridinium and (iso)quinolinium salts as described e.g. in EP 497531 and EP 441232 may be used in combination with the new photoinitiators.

The photoinitiator (B) usually is added in an amount of 0.015 to 60 parts by weight, preferably 0.03 to 30 parts by weight, based on 100 parts by weight of component (A).

The amount refers to the sum of all photoinitiators added, if mixtures of initiators are employed. Accordingly, the amount either refers to the photoinitiator (B) or the photoinitiators (B) +(B1).

The invention also pertains to compositions comprising 100 parts by weight of component (A), 0.015 to 60 parts by weight of component (B), 5 to 300 parts by weight of component (C) and 0.015 to 60 parts by weight of component (D).

The novel radiation-sensitive compositions find application as negative resists, having a very high sensitivity to light and being able to be developed in an aqueous alkaline medium without swelling. They are suitable as photoresists for electronics (electroless plating resist, electroplating resist, etch resist, solder resist).

The composition is applied uniformly to a substrate by means of known coating techniques, for example by spin coating, dip coating, knife coating, curtain coating, screen coating, brushing, spraying, especially by electrostatic spraying, and reverse-roll coating, and also by means of electrophoretic deposition. It is also possible to apply the photosensitive layer to a temporary, flexible support and then to coat the final substrate, for example a copper-clad circuit board, by transferring the layer via lamination.

The quantity applied (coat thickness) and the nature of the substrate (layer support) are dependent on the desired field of application. The range of coat thicknesses generally comprises values from about 0.1 μm to more than 100 μm , for example 0.1 μm to 1 cm, preferably 1 μm to 1000 μm .

Following the coating of the substrates, the solvent is removed, generally by drying, to leave a coat of the photoresist on the substrate.

Subject of the invention also is a solder resist comprising a composition as described above.

The term "imagewise" exposure includes both, exposure through a photomask comprising a predetermined pattern, for example a slide, as well as exposure by means of a laser or light beam, which for example is moved under computer control over the surface of the coated substrate and in this way produces an image, and irradiation with computer-controlled electron beams. It is also possible to use masks made of liquid crystals that can be addressed pixel by pixel to generate digital images, as is, for example, described by A. Bertsch, J.Y. Jezequel, J.C. Andre in *Journal of Photochemistry and Photobiology A: Chemistry* 1997, 107, p. 275-281 and by K.-P. Nicolay in *Offset Printing* 1997, 6, p. 34-37.

As already mentioned, the compositions can be developed by aqueous alkalis. Particularly suitable aqueous-alkaline developer solutions are aqueous solutions of tetraalkylammonium hydroxides or of alkali metal silicates, phosphates, hydroxides and carbonates. Minor quantities of wetting agents and/or organic solvents may also be added, if desired, to these solutions. Examples of typical organic solvents, which may be added to the developer liquids in small quantities, are cyclohexanone, 2-ethoxyethanol, toluene, acetone and mixtures of such solvents.

The photosensitivity of the novel compositions can extend in general from about 200 nm to 600 nm (UV-vis region). Suitable radiation is present, for example, in sunlight or light from artificial light sources. Consequently, a large number of very different types of light sources are employed. Both point sources and arrays ("lamp carpets") are suitable. Examples are carbon arc lamps, xenon arc lamps, medium-, high- and low-pressure mercury lamps, possibly with metal halide dopes (metal-halogen lamps), microwave-stimulated metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon incandescent lamps, electronic flashlights, photographic flood lamps, light emitting diodes (LED), electron beams and X-rays. The distance between the lamp and the substrate to be exposed in accordance with the invention may vary depending on the intended application and the type and output of lamp, and may be, for example, from 2 cm to 150 cm. Laser light sources, for example excimer lasers, such as krypton F lasers for exposure at 248 nm are also suitable. Lasers in the visible region can also be employed. By this method it is possible to produce printed circuits in the electronics industry, lithographic offset printing plates or relief printing plates, and also photographic image recording materials.

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The invention therefore also provides a process for the photopolymerization of compounds containing at least one ethylenically unsaturated double bond, which comprises adding to the abovementioned compounds at least one photoinitiator of formula I, II, III, IV or V as described above and irradiating the resulting composition with electromagnetic radiation, in particular light of the wavelength 190 to 600 nm, namely a process for the photopolymerization of compounds containing ethylenically unsaturated double bonds, which comprises irradiating a composition as described above with electromagnetic radiation in the range from 190 to 600 nm.

The invention also pertains to a coated substrate which is coated on at least one surface with a composition as described above, as well as to a process for the photographic production of relief images, in which said coated substrate is subjected to imagewise exposure with electromagnetic radiation in the range from 190 to 600 nm, and then the unexposed portions are removed with a solvent.

The compositions of the invention have a high sensitivity and resolution even at low concentration of the photoinitiator, with or without a sensitizer and are particularly suitable in aqueous developable photoresist applications. They have a good thermal stability and low volatility.

The novel radiation-sensitive compositions find application as negative resists, having a very high sensitivity to light and being able to be developed in an aqueous alkaline medium without swelling. They are suitable as photoresists for electronics like electroplating resist, etch resist, both liquid and dry films, solder resist, as resists to manufacture color filters for a variety of display applications or to generate structures in the manufacturing process of plasma-display panels and electroluminescence displays, the production of printing plates, such as offset printing plates or screen printing plates, for the production of printing forms for relief printing, planographic printing, photogravure or of screen printing forms, for the production of relief copies, for example for the production of texts in braille, for the production of stamps, for use in chemical milling or as a microresist in the production of integrated circuits. The compositions further may be used as photopatternable dielectric layer or coating, encapsulating material and isolating coating in the production of computer chips, printed boards and other electric or electronic components. The possible layer supports, and the processing conditions of the coating substrates, are just as varied.

Because the photocurable compositions according to the invention have a good thermal stability and are sufficiently resistant to inhibition by oxygen, they are particularly suitable for the production of color filters or color mosaic systems, such as described, for example, in EP 320 264. Color filters usually are employed in the manufacturing of LCD displays, projection systems and image sensors. The color filters can be used, for example, for display and image scanner in television receivers, video monitors or computers, in flat panel display technology etc..

In a process to form a color filter, the coloring matters, dyes and pigments of red, green and blue colors are added to the light-sensitive resin composition of the present invention to provide a light-sensitive resin composition layer of any color on a transparent substrate, and then it is subjected to the processes such as exposing, developing, and according to necessity, heating to form an image.

The development is carried out by washing out the areas which were not polymerized with a suitable alkali developing solution. This process is repeated to form the image having plural colors.

In the light-sensitive resin composition of the present invention, with a process in which at least one or more picture elements are formed on a transparent substrate and then an exposure is given from a side of the transparent substrate, on which the above picture elements are not formed, the above picture elements can be utilized as a light-shielding mask. In this case, for example, in the case where an overall exposure is given, a position adjustment of a mask gets unnecessary and a concern on a position slippage thereof is removed. And, it is possible to cure all of the part on which the above picture elements are not formed. Further, in this case, it is possible as well to develop and remove a part of the portion on which the above picture elements are not formed by using partially a light-shielding mask.

Since in either case, no gap is formed between the picture elements which are formed formerly and those which are formed later, the composition of the present invention is suitable for, for example, a forming material for a color filter. To be concrete, the coloring matters, dyes and pigments of red, green and blue colors are added to the light-sensitive resin composition of the present invention, and the processes for forming an image are

repeated to form the picture elements of red, green and blue colors. Then, the light-sensitive resin composition to which, for example, the black coloring materials, dyes and pigments are added is provided on an overall face. An overall exposure (or a partial exposure via a light-shielding mask) can be provided thereon to form the picture elements of a black color all over the spaces (or all but a partial region of the light-shielding mask) between the picture elements of red, green and blue colors.

In addition to a process in which the light-sensitive resin composition is coated on a substrate and dried, the light-sensitive resin composition of the present invention can be used as well for a layer transfer material. That is, the light-sensitive resin composition is layer-wise provided directly on a temporary support, preferably on a polyethylene terephthalate film, or on a polyethylene terephthalate film on which an oxygen-shielding layer and a peeling layer or the peeling layer and the oxygen-shielding layer are provided. Usually, a removable cover sheet made of a synthetic resin is laminated thereon for a protection in handling. Further, there can be applied as well a layer structure in which an alkali soluble thermoplastic resin layer and an intermediate layer are provided on a temporary support and further a light-sensitive resin composition layer is provided thereon (JP-A-5-173320).

The above cover sheet is removed in use and the light-sensitive resin composition layer is laminated on a permanent support. Subsequently, peeling is carried out between those layer and a temporary support when an oxygen-shielding layer and a peeling layer are provided, between the peeling layer and the oxygen-shielding layer when the peeling layer and the oxygen-shielding layer are provided, and between the temporary support and the light-sensitive resin composition layer when either the peeling layer or the oxygen-shielding layer is not provided, and the temporary support is removed.

A metal support, glass, ceramics, and a synthetic resin film can be used as a support for a color filter. Glass and a synthetic resin film which is transparent and have an excellent dimension stability is particularly preferred.

The thickness of the light-sensitive resin composition layer is usually 0.1 to 50 micrometers, in particular 1 to 5 micrometers.

A diluted aqueous solution of an alkaline substance is used as a developing solution for the light-sensitive resin composition of the present invention, and further a solution prepared by adding a small amount of a water-miscible organic solvent thereto is included as well.

Examples of suitable alkaline materials include alkali metal hydroxides (for example, sodium hydroxide and potassium hydroxide), alkali metal carbonates (for example, sodium carbonate and potassium carbonate), alkali metal bicarbonates (for example, sodium bicarbonate and potassium bicarbonate), alkali metal silicates (for example, sodium silicate and potassium silicate), alkali metal metasilicates (for example, sodium metasilicate and potassium metasilicate), triethanolamine, diethanolamine, monoethanolamine, morpholine, tetraalkylammonium hydroxides (for example, tetramethylammonium hydroxide), or trisodium phosphate. The concentration of the alkaline substance is 0.01 to 30 weight %, and pH is preferably 8 to 14.

Suitable organic solvents which are miscible with water include methanol, ethanol, 2-propanol, 1-propanol, butanol, diacetonealcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, benzyl alcohol, acetone, methyl ethyl ketone, cyclohexanone, epsilon-caprolactone, gamma-butyrolactone, dimethylformamide, dimethylacetamide, hexamethylphosphoramide, ethyl lactate, methyl lactate, epsilon-caprolactam, and N-methyl-pyrrolidone. The concentration of the organic solvent which is miscible with water is 0.1 to 30 weight %.

Further, a state of the art surface active agent known to the person skilled in the art can be added. The concentration of the surface active agent is preferably 0.001 to 10 weight %.

The developing solution can be used in either form of a bath solution or a spraying solution. In order to remove the non-cured portion of the light-sensitive resin composition layer, there can be combined the methods such as rubbing with a rotary brush and rubbing with a wet sponge. Usually, the temperature of the developing solution is preferably at and around room temperature to 40°C. The developing time is changeable according to the specific kind of the light-sensitive resin composition, the alkalinity and temperature of the developing solution, and the kind and concentration of the organic solvent in the case where it is added. Usually, it is 10 seconds to 2 minutes. It is possible to put a rinsing step after the development processing.

A final heat treatment is preferably carried out after the development processing. Accordingly, a support having a layer which is photopolymerized by exposing (hereinafter referred to as a photocured layer) is heated in an electric furnace and a drier, or the photocured layer is irradiated with an infrared lamp or heated on a hot plate. The heating temperature and time depend on the composition used and the thickness of the formed layer. In general, heating is preferably applied at about 120°C to about 250°C, for about 5 to about 60 minutes.

The light-sensitive composition of the present invention can suitably be used for forming a color filter but will not be limited to this application. It is useful as well for other applications, e.g. recording materials, displays, display elements, paints, and printing inks.

Because the photocurable compositions according to the invention have a good thermal stability and are sufficiently resistant to inhibition by oxygen, they are particularly suitable for the production of color filters or color mosaic systems, such as described, for example, in EP 320 264. Color filters usually are employed in the manufacturing of LCD displays, projection systems and image sensors. The color filters usually are prepared by forming red, green and blue pixels and a black matrix on a glass substrate. In these processes photocurable compositions according to the invention can be employed. A particularly preferred method of use comprises the coating of the substrate with the composition of the invention, drying of the coating with a short heat treatment, patternwise exposure of the coating to actinic radiation and subsequent development of the pattern in an aqueous alkaline developer solution and optionally a heat treatment. Thus, by subsequently applying a red, green and blue pigmented coating, in any desired order, on top of each other with this process a color filter layer with red, green and blue color pixels can be produced. The color filters can be used, for example, for display and image scanner in television receivers, video monitors or computers, in flat panel display technology etc..

The pigment which can be comprised in the composition according to the present invention, including a pigmented color filter resist composition, is preferably a processed pigment, for example a powdery or pasty product prepared by finely dispersing a pigment into at least one resin selected from the group consisting of acrylic resin, vinyl chloride-vinyl acetate copolymer, maleic acid resin and ethyl cellulose resin.

The red pigment comprises, for example, an anthraquinone type pigment alone, a perylene type pigment alone, or a mixture consisting of at least one of them and a disazo type yellow pigment or an isoindoline type yellow pigment, in particular C. I. Pigment Red 177 alone, C. I. Pigment Red 155 alone or a mixture consisting of at least one member of C. I. Pigment Red 177, C. I. Pigment Red 155 and C. I. Pigment Yellow 83 or C. I. Pigment Yellow 139 ("C.I." refers to the Color Index, known to the person skilled in the art and publicly available).

Further suitable examples for the pigment are C.I. Pigment Red 105, 144, 149, 176, 177, 185, 202, 209, 214, 222, 242, 254, 255, 264, 272 and C.I. Pigment Yellow 24, 31, 53, 83, 93, 95, 109, 110, 128, 129, 138, 139, 166 and C.I. Pigment Orange 43.

The green pigment comprises for instance a halogenated phthalocyanine type pigment alone or its mixture with a disazo type yellow pigment or an isoindoline type yellow pigment, in particular C. I. Pigment Green 7 alone, C. I. Pigment Green 36 alone, C. I. Pigment Green 37 alone or a mixture consisting of at least one member of C. I. Pigment Green 7, C. I. Pigment Green 36, C. I. Pigment Green 37, C.I. Pigment Green 136 and C. I. Pigment Yellow 83 or C. I. Pigment Yellow 139. Other suitable green pigments are C.I. Pigment Green 15 and 25.

Examples for suitable blue pigments are phthalocyanine type pigments, used either alone or in combination with a dioxazine type violet pigment, for instance, a combination of C. I. Pigment Blue 15:3 and C. I. Pigment Violet 23. Further examples for blue pigments are such of C.I. Blue 15:3, 15:4, 15:6, 16 and 60, i.e. Phthalocyanine C.I. Pigment Blue 15:3, or Phthalocyanine C.I. Pigment Blue 15:6. Other suitable pigments are such of C.I. Pigment Blue 22, 28, C.I. Pigment Violet 14, 19, 23, 29, 32, 37, 177 and C.I. Orange 73.

The pigment of the black matrix photopolymeric composition preferably comprises at least one member selected from the group consisting of carbon, titanium black and iron oxide. However, a mixture of other pigments which, in total, give the black appearance, can also be used. For example, also C.I. Pigment Black 1 and 7 can be used alone or in combination.

For any color, combinations of more than two pigments can also be used. Especially suitable in color filter applications are powdery processed pigments prepared by finely dispersing the above mentioned pigments into a resin.

The concentration of the pigment in the total solid component (pigments of various colors and resin) is for example in the range of 5% to 80% by weight, in particular in the range of 20% to 40% by weight.

The pigments in the color filter resist composition have preferably a mean particle diameter smaller than the wavelength of visible light (400 nm to 700 nm). Particularly preferred is a mean pigment diameter of < 100 nm.

The concentration of the pigment in the total solid component in each color is in the range from 5% by weight to 80% by weight, preferably in the range of 20% to 45%.

If necessary, the pigments may be stabilized in the photosensitive composition by pretreatment of the pigments with a dispersant to improve the dispersion stability of the pigment in the liquid formulation.

Examples for color filter resists, the composition of such resists and the processing conditions are given by T. Kudo et al., Jpn. J. Appl. Phys. Vol. 37 (1998) 3594; T. Kudo et al., J. Photopolym. Sci. Technol. Vol 9 (1996) 109; K. Kobayashi, Solid State Technol. Nov. 1992, p. S15-S18; US 5368976; US 5800952; US 5882843; US 5879855; US 5866298; US 5863678; JP 06-230212-A; EP 320264; JP 09-269410-A; JP 10-221843-A; JP 01-090516-A; JP 10-171119-A, US 5821016, US 5847015, US 5882843, US 5719008, EP 881541, or EP 902327.

The photoinitiators of the present invention can be used in color filter resists, for example, such as those given as examples above, or can partially or fully replace the known photoinitiators in such resists. It is understood by a person skilled in the art that the use of the new photoinitiators of the present invention is not limited to the specific binder resins, crosslinkers and formulations of the color filter resist examples given hereinbefore but can be used in conjunction with any radically polymerizable component in combination with a dye or color pigment or latent pigment to form a photosensitive color filter ink or color filter resist.

Accordingly, subject of the invention also is a color filter prepared by providing red, green and blue (RGB) colour elements and, optionally a black matrix, all comprising a photosensitive resin and a pigment on a transparent substrate and providing a transparent electrode either on the surface of the substrate or on the surface of the color filter layer, wherein said photosensitive resin comprises a polyfunctional acrylate monomer, an organic

polymer binder and a photopolymerization initiator of formula I, II, III, IV or V as described above. The monomer and binder components, as well as suitable pigments are as described above. In the manufacture of color filters the transparent electrode layer can either be applied on the surface of the transparent substrate or can be provided on the surface of the red, green and blue picture elements and the black matrix. The transparent substrate is for example a glass substrate which can additionally have an electrode layer on its surface.

It is preferred to apply a black matrix between the color areas of different color in order to improve the contrast of a color filter.

Instead of forming a black matrix using a photosensitive composition and patterning the black photosensitive composition photolithographically by patternwise exposure (i.e. through a suitable mask) to form the black pattern separating the red green and blue coloured areas on the transparent substrate it is alternatively possible to use an inorganic black matrix. Such inorganic black matrix can be formed from deposited (i.e. sputtered) metal (i.e. chromium) film on the transparent substrate by a suitable imaging process, for example utilizing photolithographic patterning by means of an etch resist, etching the inorganic layer in the areas not protected by the etch resist and then removing the remaining etch resist.

There are different methods known how and at which step in the color filter manufacturing process the black matrix can be applied. It can either be applied directly on the transparent substrate prior to formation of the red, green and blue (RGB) colour filter as already mentioned above, or it can be applied after the RGB colour filter is formed on the substrate.

In a different embodiment of a color filter for a liquid crystal display, according to US 5626796, the black matrix can also be applied on the substrate opposite to the RGB color filter element-carrying substrate, which is separated from the former by a liquid crystal layer.

If the transparent electrode layer is deposited after applying the RGB color filter elements and -optionally - the black matrix, an additional overcoat film as a protective layer can be applied on the color filter layer prior to deposition of the electrode layer, for example, as described in US 5650263.

It is obvious to those skilled in the art, that the photosensitive compositions of the present invention can be used for generating red, green and blue color pixels and a black matrix, for the manufacture of a color filter, regardless of the above described differences in processing, regardless, of additional layers which can be applied and regardless of differences in the design of the color filter. The use of a composition according to the present invention to form colored elements shall not be regarded as limited by different designs and manufacturing processes of such color filters.

Preferably, the organic polymer binder in the color filter resist composition comprises an alkali soluble copolymer comprising, as addition polymerizable monomer units, at least an unsaturated organic acid compound such as acrylic acid, methacrylic acid and the like. It is preferred to use as a further co-monomer for the polymer binder an unsaturated organic acid ester compound such as methyl acrylate, ethyl (meth)acrylate, benzyl (meth)acrylate, styrene and the like to balance properties such as alkaline solubility, adhesion rigidity, chemical resistance etc..

The organic polymer binder can either be a random co-polymer or a block-co-polymer, for example, such as described in US 5368976.

Preferably, the color filter resist composition according to the present invention contains additionally at least one addition polymerizable monomeric compound.

For example, the following compounds can be used singly or in combination with the other monomers as the addition-polymerizable monomer having an ethylenically unsaturated double bond used in the present invention. Specifically, they include t-butyl(meth)acrylate, ethylene glycol di(meth)acrylate, 2-hydroxypropyl (meth)acrylate, triethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 2-ethyl-2-butylpropanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, polyoxyethylated trimethylolpropane tri(meth)acrylate, tris(2-(meth)acryloyloxyethyl)isocyanurate, 1,4-diisopropenyl-benzene, 1,4-dihydroxybenzene (meth)acrylate, decamethylene glycol di(meth)acrylate, styrene, diallyl fumarate, triallyl trimellitate, lauryl (meth)acrylate, (meth)acrylamide, and xylenebis(meth)acrylamide. Further, there can be used a reaction product of a compound having a hydroxyl group, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and polyethylene glycol mono(meth)acrylate with diisocyanate such as hexamethylenediisocyanate, toluenediisocyanate, and xylenediisocyanate. Particularly

preferred are pentaerythritol tetra-acrylate, dipentaerythritol hexaacrylate, dipenta-erythritol pentaacrylate, and tris(2-acyloyloxyethyl)-isocyanurate.

In a color filter resist composition the whole amount of the monomers contained in the photopolymerizable composition is preferably 5 to 80 % by weight, in particular 10 to 70 % by weight based on the whole components of the composition.

As the binder used in the color filter resist composition, which is soluble in an alkaline aqueous solution and insoluble in water, for example, a homopolymer of a polymerizable compound having one or more acid groups and one or more polymerizable unsaturated bonds in the molecule, or a copolymer of two or more kinds thereof, and a copolymer of one or more polymerizable compounds having one or more unsaturated bonds copolymerizable with these compounds and containing no acid group, can be used. Such compounds can be obtained by copolymerizing one or more kinds of a low molecular compound having one or more acid groups and one or more polymerizable unsaturated bonds in the molecule with one or more polymerizable compounds having one or more unsaturated bonds copolymerizable with these compounds and containing no acid group. Examples of acids groups are, a -COOH group, a $\text{-SO}_3\text{H}$ group, a $\text{-SO}_2\text{NHCO-}$ group, a phenolic hydroxy group, a $\text{-SO}_2\text{NH-}$ group, and a -CO-NH-CO- group. Among those, a high molecular compound having a -COOH group is particularly preferred.

Examples of polymerizable compounds having one or more acid group and one or more polymerizable unsaturated bond in the molecule include the following compounds:

Acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, vinylbenzoic acid, and cinnamic acid are examples of the polymerizable compounds having one or more -COOH groups and one or more polymerizable unsaturated bonds in a molecule.

Vinylbenzenesulfonic acid and 2-(meth)acrylamide-2-methylpropanesulfonic acid are examples of the polymerizable compounds having one or more $\text{-SO}_3\text{H}$ groups and one or more polymerizable unsaturated bonds.

N-methylsulfonyl (meth)acrylamide, N-ethylsulfonyl (meth)acrylamide, N-phenylsulfonyl (meth)acrylamide, and N-(p-methylphenylsulfonyl) (meth)acrylamide are examples of the polymerizable compounds having one or more $\text{-SO}_2\text{NHCO-}$ groups and one or more polymerizable unsaturated bonds.

Examples of polymerizable compounds having one or more phenolic hydroxy groups and one or more polymerizable unsaturated bonds in a molecule include hydroxyphenyl (meth)acrylamide, dihydroxyphenyl (meth)acrylamide, hydroxyphenyl-carbonyloxyethyl (meth)acrylate, hydroxyphenyloxyethyl (meth)acrylate, hydroxyphenylthioethyl (meth)acrylate, dihydroxyphenylcarbonyloxyethyl (meth)acrylate, dihydroxyphenyloxyethyl (meth)acrylate, and dihydroxyphenylthioethyl (meth)acrylate.

Examples of the polymerizable compound having one or more $-\text{SO}_2\text{NH}-$ groups and one or more polymerizable unsaturated bonds in the molecule include compounds represented by formula (a) or (b):



wherein Y_1 and Y_2 each represents $-\text{COO}-$, $-\text{CONA}_7-$, or a single bond; A_1 and A_4 each represents H or CH_3 ; A_2 and A_5 each represents C_1 - C_{12} alkylene optionally having a substituent, cycloalkylene, arylene, or aralkylene, or C_2 - C_{12} alkylene into which an ether group and a thioether group are inserted, cycloalkylene, arylene, or aralkylene; A_3 and A_6 each represents H, C_1 - C_{12} alkyl optionally having a substituent, a cycloalkyl group, an aryl group, or an aralkyl group; and A_7 represents H, C_1 - C_{12} alkyl optionally having a substituent, a cycloalkyl group, an aryl group, or an aralkyl group.

The polymerizable compounds having one or more $-\text{CO-NH-CO}-$ group and one or more polymerizable unsaturated bond include maleimide and N-acryloyl-acrylamide. These polymerizable compounds become the high molecular compounds comprising a $-\text{CO-NH-CO}-$ group, in which a ring is formed together with a primary chain by polymerization. Further, a methacrylic acid derivative and an acrylic acid derivative each having a $-\text{CO-NH-CO}-$ group can be used as well. Such methacrylic acid derivatives and the acrylic acid derivatives include, for example, a methacrylamide derivative such as N-acetylmethacrylamide, N-propionylmethacrylamide, N-butanoylmethacrylamide, N-pentanoylmethacrylamide, N-decanoylmethacrylamide, N-dodecanoylmethacrylamide, N-benzoylmethacrylamide, N-(p-methylbenzoyl)methacrylamide, N-(p-chlorobenzoyl)methacrylamide, N-(naphthyl-carbonyl)methacrylamide, N-(phenylacetyl)methacrylamide, and 4-methacryloylaminophthalimide, and an acrylamide derivative having the same substituent as these. These polymerizable compounds polymerize to be compounds having a $-\text{CO-NH-CO}-$ group in a side chain.

Examples of polymerizable compounds having one or more polymerizable unsaturated bond and containing no acid group include a compound having a polymerizable unsaturated bond, selected from (meth)acrylates, (meth)acrylamides, an acrylic compound, vinyl ethers, vinyl esters, styrenes, and crotonates, and specifically, include (meth)acrylates such as alkyl (meth)acrylate or substituted alkyl (meth)acrylate (for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, ethylhexyl (meth)acrylate, octyl (meth)acrylate, t-octyl (meth)acrylate, chloro-ethyl (meth)acrylate, allyl (meth)acrylate, 2-hydroxy-ethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2,2-dimethyl-3-hydroxy-propyl (meth)acrylate, 5-hydroxypentyl (meth)acrylate, trimethylolpropane mono (meth)acrylate, pentaerythritol mono (meth)acrylate, benzyl (meth)acrylate, methoxy-benzyl (meth)acrylate, chlorobenzyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, phenoxyethyl (meth)acrylate, and aryl (meth)acrylate (for example, phenyl (meth)acrylate, cresyl (meth)acrylate, and naphthyl (meth)acrylate); (meth)acrylamides such as (meth)acryl-amide, N-alkyl(meth)acrylamide (the alkyl group includes, for example, methyl, ethyl, propyl, butyl, t-butyl, heptyl, octyl, ethylhexyl, cyclohexyl, hydroxy-ethyl, and benzyl), N-aryl(meth)acrylamide (the aryl group includes, for example, phenyl, tolyl, nitrophenyl, naphthyl, and hydroxyphenyl), N,N-dialkyl(meth)acrylamide (the alkyl group includes, for example, methyl, ethyl, butyl, isobutyl, ethylhexyl, and cyclohexyl), N,N-diaryl (meth)acrylamide (the aryl group includes, for example, phenyl), N-methyl-N-phenyl (meth)acryl-amide, N-hydroxyethyl-N-methyl (meth)acrylamide, N-2-acetoamidethyl-N-acetyl(meth)acrylamide, N-(phenyl-sulfonyl)(meth)acrylamide, and N-(p-methylphenyl-sulfonyl)(meth)acrylamide; an allyl compound such as allyl esters (for example, allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, and allyl lactate), and allyloxyethanol; vinyl ethers such as alkyl vinyl ether (the alkyl group includes, for example, hexyl, octyl, decyl, ethylhexyl, methoxyethyl, ethoxyethyl, chloroethyl, 1-methyl-2,2-dimethylpropyl, 2-ethylbutyl, hydroxyethyl, hydroxyethoxyethyl, dimethylaminoethyl, diethylamino-ethyl, butylaminoethyl, benzyl, and tetrahydrofurfuryl), and vinyl aryl ether (the aryl group includes, for example, phenyl, tolyl, chlorophenyl, 2,4-dichloro-phenyl, naphthyl, and anthranyl); vinyl esters such as vinyl butylate, vinyl isobutylate, vinyl trimethylacetate, vinyl diethyl-acetate, vinyl barate, vinyl caproate, vinyl chloro-acetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl phenylacetate, vinyl aceto-acetate, vinyl lactate,

vinyl-b-phenylbutylate, vinyl cyclohexylcarboxylate, vinyl benzoate, vinyl salicylate, vinyl chlorobenzoate, vinyl tetrachlorobenzoate, and vinyl naphthoate;

styrenes such as styrene, alkylstyrene (for example, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, benzylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, and acetoxymethylstyrene), alkoxy styrene (for example, methoxystyrene, 4-methoxy-3-methylstyrene, and dimethoxystyrene), and halogenostyrene (for example, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, penta-chlorostyrene, bromostyrene, dibromostyrene, iodostyrene, fluorostyrene, trifluorostyrene, 2-bromo-4-trifluoromethylstyrene, and 4-fluoro-3-trifluoromethylstyrene);

crotonates such as alkyl crotonate (for example, butyl crotonate, hexyl crotonate, and glycerine monocrotonate);

dialkyl itaconates (for example, dimethyl itaconate, diethyl itaconate, and dibutyl itaconate);

dialkyl maleates or fumarates (for example, dimethyl maleate and dibutyl fumarate); and (meth)acrylonitrile.

There can be used as well hydroxystyrene homo- or co-polymers or a novolak type phenol resin, for example, poly(hydroxystyrene) and poly(hydroxystyrene-co-vinylcyclohexanol), a novolak resin, a cresol novolak resin, and a halogenated phenol novolak resin. More specifically, it includes, for example, the methacrylic acid copolymers, the acrylic acid copolymers, the itaconic acid copolymers, the crotonic acid copolymers, the maleic anhydride co-polymers, for example, with styrene as a co-monomer, and maleic acid copolymers, and partially esterified maleic acid copolymers each described in, for example, JP 59-44615-B4 (the term "JP-B4" as used herein means an examined Japanese patent publication), JP 54-34327-B4, JP 58-12577-B4, and JP 54-25957-B4, JP 59-53836-A, JP 59-71048-A, JP 60-159743-A, JP 60-258539-A, JP 1-152449-A, JP 2-199403-A, and JP 2-199404-A, and which copolymers can be further reacted with an amine, as e.g. disclosed in US 5650263; further, a cellulose derivative having a carboxyl group on a side chain can be used, and particularly preferred are copolymers of benzyl (meth)acrylate and (meth)acrylic acid and copolymers of benzyl (meth)acrylate, (meth)acrylic acid and other monomers, for example as described in US 4139391, JP 59-44615-B4, JP 60-159743-A and JP 60-258539-A.

With respect to those having carboxylic acid groups among the above organic binder polymers, it is possible to react some or all of the carboxylic acid groups with glycidyl(meth)acryl-

ate or an epoxy(meth)acrylate to obtain photopolymerizable organic binder polymers for the purpose of improving the photosensitivity, coating film strength, the coating solvent and chemical resistance and the adhesion to the substrate. Examples are disclosed in, JP 50-34443-B4 and JP 50-34444-B4, US 5153095, by T. Kudo et al. in J. Appl. Phys., Vol. 37 (1998), p. 3594-3603, US 5677385, and US 5650233.

The weight-average molecular weight of the binders is preferably 500 to 1'000'000, e.g. 3'000 to 1'000'000, more preferably 5'000 to 400'000.

These compounds may be used singly or as a mixture of two or more kinds. The content of the binder in the light-sensitive resin composition is preferably 10 to 95 weight %, more preferably 15 to 90 weight % based on the whole solid matters.

Further, in the color filter the total solid component of each color may contain an ionic impurity-scavenger, e.g. an organic compound having an epoxy group. The concentration of the ionic impurity scavenger in the total solid component generally is in the range from 0.1% by weight to 10% by weight.

Examples of color filters, especially with respect to the above described combinations of pigments and ionic impurity scavenger are given in EP 320264. It is understood, that the photoinitiators according to the present invention, i.e. the compounds of the formula I, II, III, IV and V in the color filter formulations described in EP 320264 can replace the triazine initiator compounds.

The compositions according to this invention can comprise additionally a crosslinking agent which is activated by an acid, for example as described in JP 10 221843-A, and a compound which generates acid thermally or by actinic radiation and which activates a crosslinking reaction.

The compositions according to this invention can also comprise latent pigments which are transformed into finely dispersed pigments during the heat treatment of the latent pigment containing photosensitive pattern or coating. The heat treatment can be performed after exposure or after development of the latent pigment-containing photoimageable layer. Such latent pigments are soluble pigment precursors which can be transformed into insoluble pigments by means of chemical, thermal, photolytic or radiation induced methods as described, for example, in US 5879855. This transformation of such latent pigments can be enhanced

by adding a compound which generates acid at actinic exposure or by adding an acidic compound to the composition. Therefore, a color filter resist can also be prepared, which comprises a latent pigment in a composition according to this invention.

Following the coating of the substrates, the solvent is removed, generally by drying, to leave an essentially dry resist film of the photoresist on the substrate.

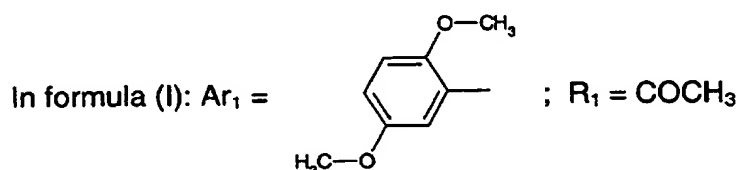
Another preferred use of the compositions according to the invention is an image-forming process, e.g. a process for the preparation of solder masks, wherein

- (1) the components of the composition as described above are mixed
- (2) the resulting composition is applied to the substrate ("coating of the substrate")
- (3) the solvent, if present, is evaporated, at elevated temperature, e.g. at a temperature between 80-90°C
- (4) the coated substrate is exposed to electromagnetic radiation through a negative mask (thereby initiating the reaction of the acrylate)
- (5) the irradiated sample is developed, by washing with aqueous alkaline solution and thereby removing the uncured areas and
- (6) the sample is thermally cured, e.g. at a temperature about 150°C, thereby initiating the crosslinking between the carboxylic acid and the epoxy component.

This process is another object of the invention.

The examples which follow illustrate the invention in more detail. Parts and percentages are, as in the remainder of the description and in the claims, by weight, unless stated otherwise. Where alkyl radicals having more than three carbon atoms are referred to without any mention of specific isomers, the n-isomers are meant in each case.

Example 1: Synthesis of 2,5-Dimethoxybenzaldehyde oxime-O-acetate



1.a 2,5-Dimethoxybenzaldehyde oxime

To 16.6 g (99.9 mmol) of 2,5-dimethoxybenzaldehyde in ethanol (100 mL) is added a mixture of 7.64 g (169 mmol) of $H_2NOH-HCl$ and 13.9 g (169 mmol) of sodium acetate in 50 mL of

H₂O. This reaction mixture is heated to reflux for 2.5h. After adding H₂O to dissolve the precipitated inorganic salt, ethanol is removed by evaporation in vacuo. The resulting white solid is filtered off and washed with H₂O. 14.9 g of white solid are obtained (82%). ¹H-NMR (CDCl₃). δ [ppm]: 3.79 (s, 3H), 3.82 (s, 3H), 6.85 (d, 1H), 6.92 (d, 1H), 7.25 (d, 1H), 8.00 (broad s, 1H), 8.47 (s, 1H).

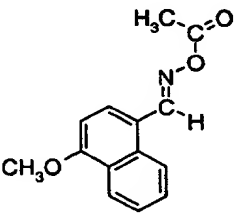
1.b 2,5-Dimethoxybenzaldehyde oxime-O-acetate

2.00 g (11.0 mmol) of 2,5-Dimethoxybenzaldehyde oxime and 1.13 g (14.3 mmol) of acetyl chloride are dissolved in 15 mL of tetrahydrofuran (THF). To this solution are gradually added 1.67 g (16.5 mmol) of triethylamine at an ice-bath temperature. After completion of the addition, the reaction mixture is stirred at room temperature for 3h, and then H₂O is added to dissolve the resulting white solid. The crude product is extracted with ethyl acetate. This organic layer is washed twice with saturated NaHCO₃ aq. solution and with brine, followed by drying over anhydrous MgSO₄. The residue is applied to column chromatography on silica gel with ethyl acetate - hexane (1:4) as eluent. 2.03 g of white solid melting at 55 - 57°C are obtained (83%). The structure is confirmed by the ¹H-NMR spectrum (CDCl₃). δ [ppm]: 2.23 (s, 3H), 3.81 (s, 3H), 3.83 (s, 3H), 6.87 (d, 1H), 7.01 (dd, 1H), 7.47 (d, 1H), 8.75 (s, 1H).

Examples 2 - 10:

The compounds of examples 2-10 are prepared according to the method described in example 1 from the corresponding aldehydes. The compounds and their ¹H-NMR-data are given in table 1.

Table 1

Example	structure	state/ mp [°C]	¹ H-NMR, δ [ppm]
2		99-101	2.27 (s, 3H), 4.05 (s, 3H), .84 (d, 1H), 7.54 (t, 1H), 7.65 (t, 1H), 7.81 (d, 1H), 8.33 (d, 1H), 8.64 (d, 1H), 8.85 (s, 1H)

Example	structure	state/ mp [°C]	¹ H-NMR, δ [ppm]
3		colorless liquid	2.23 (s, 3H), 3.39 (s, 3H), 3.94 (s, 3H), 6.88 (d, 1H), 7.14 (d, 1H), 7.39 (s, 1H), 8.23 (s, 1H)
4		colorless liquid	2.22 (s, 3H), 3.85 (s, 3H), 6.93 (d, 2H), 7.69 (d, 2H), 8.30 (s, 1H)
5		104-107	2.22 (s, 3H), 6.03 (s, 2H), 6.84 (d, 1H), 7.09 (d, 1H), 7.36 (s, 1H), 8.25 (s, 1H)
6		colorless liquid	2.22 (s, 3H), 3.87 (s, 3H), 6.92 (d, 1H), 6.98 (dd, 1H), 7.43 (dd, 1H), 7.97 (d, 1H), 8.77 (s, 1H)
7		colorless liquid	2.24 (s, 3H), 7.38-7.52 (m, 3H), 7.74 (d, 2H), 8.36 (s, 1H)
8		54-56	2.25 (s, 3H), 2.47 (s, 3H), 7.21-7.26 (m, 2H), 7.36 (dt, 1H), 7.84 (d, 1H), 8.62 (s, 1H)

Example	structure	state/ mp [°C]	¹ H-NMR, δ [ppm]
9		83-84	2.30 (s, 3H), 7.50-7.59 (m, 2H), 7.65 (t, 1H), 7.91 (d, 2H), 7.98 (d, 2H), 8.57 (d, 1H), 8.99 (s, 1H)
10		58-59	1.23 (t, 3H), 2.49 (q, 2H), 3.85 (s, 3H), 6.93 (d, 2H), 7.68 (d, 2H), 8.30 (s, 1H)
11		103-106	2.21 (s, 3H), 3.03 (s, 6H), 6.68 (d, 2H), 7.59 (d, 2H), 8.23 (s, 1H)

The following sensitizers are used in examples 12 and 13:

S-1 a mixture of 2-isopropylthioxanthone and 4-isopropylthioxanthone (^{RTM}QUANTACURE ITX, provided by International Biosynthetics) S-2

S-2 4,4'-bis(diethylamino)benzophenone (Michler's ketone)

Example 12

A photocurable formulation for a sensitivity test is prepared by mixing the following components:

200.0 parts by weight of acrylated acrylicopolymer (^{RTM}ACA200M, provided by Daicel Industries, Ltd., solid content is 50% by weight)

15.0 parts by weight of dipentaerythritol hexaacrylate ((DPHA), provided by UCB Chemicals),

100.0 parts by weight of acetone

To that mixture 0.5 % (based on the solid content) of S-1 and 2% (based on the solid content) of the initiator to be tested are added and stirred. All operations are carried out under yellow light. The formulations are applied to an aluminum plate. The solvent is removed by heating at 80 C° for 15 minutes in a convection oven. The thickness of the dry film is 25 µm. Onto this coating an acetate film is applied, over which a standardized test negative with 21 steps of different optical density (Stouffer step wedge) is placed. The sample is covered with a second UV-transparent film and pressed onto a metal plate by means of vacuum. Exposure is carried out in a first test series for 40 seconds, in a second series for 80 seconds and in a third series for 160 seconds, using a metal halide lamp (ORC, model SMX 3000) at a distance of 60 cm. Following exposure, the cover films and the mask are removed and the exposed film is developed with 1% sodium carbonate aqueous solution for 180 sec. at 30°C by using a spray type developer (Walter Lemmen, model T21). The sensitivity of the initiator system used is characterized by indicating the highest step number which remained (i.e. polymerized) after developing. The higher the number of steps, the more sensitive is the system tested.

The results are collected in table 2.

Table 2

Photoinitiator of example	Number of steps reproduced after exposure time of		
	40 sec.	80 sec.	160 sec.
1	11	13	15
2	11	13	15
3	10	13	14
4	9	12	14
5	10	12	14
6	9	11	13
7	8	10	12
8	8	10	12
9	8	10	12

Example 13

Preparation of Poly(benzylmethacrylate-co-methacrylic acid)

24 g of benzylmethacrylate, 6 g of methacrylic acid and 0.525 g of azobisisobutyronitrile (AIBN) are dissolved in 90 ml of propylene glycol 1-monomethyl ether 2-acetate (PGMEA).

The resulting reaction mixture is placed in a preheated oil bath at 80°C. After stirring for 5 hours at 80°C under nitrogen, the resulting viscous solution is cooled to room temperature and used without further purification. The solid content is about 25%.

A photocurable composition is prepared by mixing the following components:

- 240.0 parts by weight of copolymer of benzylmethacrylate and methacrylic acid
(benzylmethacrylate : methacrylic acid = 80 : 20 by weight)
- 25% propylene glycol 1-monomethyl ether 2-acetate
(PGMEA) solution, prepared as described above
- 40.0 parts by weight of dipentaerythritol hexaacrylate ((DPHA), provided by UCB
Chemicals),
- 2.0 parts by weight of the photoinitiator,
- 1.2 parts by weight of the sensitizer, and
- 120.0 parts by weight of PGMEA

All operations are carried out under yellow light. The compositions are applied to an aluminum plate using an electric applicator with a wire wound bar. The solvent is removed by heating at 100°C for 2 minutes in a convection oven. The thickness of the dry film is approximately 2 µm. A standardized test negative film with 21 steps of different optical density (Stouffer step wedge) is placed with an air gap of around 100 µm between the film and the resist. Exposure is carried out using a 250W super high pressure mercury lamp (USHIO, USH-250BY) at a distance of 15 cm. A total exposure dose measured by an optical power meter (ORC UV Light Measure Model UV-M02 with UV-35 detector) on the test negative film is 500mJ/cm². After exposure, the exposed film is developed with 1% sodium carbonate aqueous solution for 100 sec. at 30°C by using a spray type developer (Walter Lemmen, model T21). The sensitivity of the initiator system used is characterized by indicating the highest number of the step remaining (i.e. polymerized) after developing. The higher the number of steps, the more sensitive is the system tested. The results are listed in table 3.

Table 3

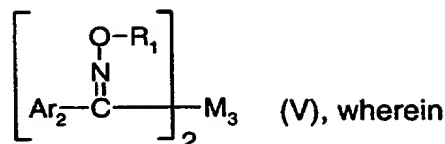
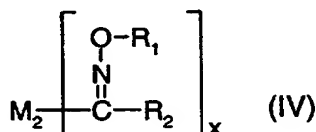
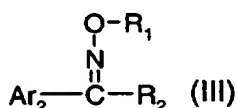
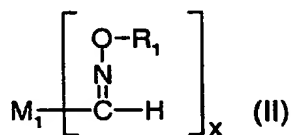
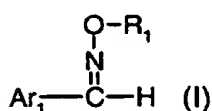
Photoinitiator of example	Sensitizer	Number of steps reproduced after exposure of 500mJ/cm ²
4	S-1	9
4	S-2	11
3	S-1	10
3	S-2	11
6	S-1	9

Photoinitiator of example	Sensitizer	Number of steps reproduced after exposure of 500mJ/cm ²
6	S-2	11
10	S-1	7
10	S-2	10
2	S-1	10
2	S-2	12
5	S-1	10
5	S-2	13
11	S-1	9
11	S-2	11
1	S-1	10
1	S-2	12

Patent Claims

1. Photosensitive composition comprising

- (A) an oligomer or polymer containing at least one carboxylic acid group in the molecule;
 (B) at least one compound of formula I, II, III, IV or V



R₁ is C₄-C₉cycloalkanoyl, C₃-C₁₂alkenoyl; C₁-C₂₀alkanoyl which is unsubstituted or substituted by one or more halogen, CN or phenyl; or R₁ is benzoyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, halogen, CN, OR₃, SR₄ or NR₅R₆; or R₁ is C₂-C₁₂alkoxycarbonyl or phenoxycarbonyl which is unsubstituted or substituted by one or more C₁-C₆alkyl or halogen;

R₂ is phenyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, phenyl, halogen, OR₃, SR₄ or NR₅R₆; or R₂ is C₁-C₂₀alkyl, C₂-C₂₀alkenyl, C₂-C₂₀alkynyl; or C₂-C₂₀alkyl optionally interrupted by one or more -O- and/or optionally substituted by one or more halogen, OH, OR₃, phenyl or phenyl substituted by OR₃, SR₄ or NR₅R₆; or R₂ is C₃-C₈cycloalkyl, C₂-C₂₀alkanoyl; or benzoyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, phenyl, OR₃, SR₄ or NR₅R₆; or R₂ is C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups; or R₂ is phenoxycarbonyl which is unsubstituted or substituted by C₁-C₆alkyl, halogen, phenyl, OR₃ or NR₅R₆; or R₂ is -CONR₅R₆, CN, NO₂, C₁-C₄haloalkyl, S(O)_mC₁-C₆alkyl, unsubstituted or C₁-C₁₂alkyl-substituted S(O)_m-C₆-C₁₂aryl, SO₂O-C₁-C₆alkyl, SO₂O-C₆-C₁₀aryl, or diphenyl-phosphinoyl, or R₂ may form 5- or 6-membered rings with one of the carbon atoms of the aromatic ring;

m is 1 or 2;

Ar₁ is either C₆-C₂₀aryl or C₆-C₂₀aryloyl,

each of these radicals is unsubstituted or substituted 1 to 12 times by halogen, C₁-C₁₂alkyl, benzyl, benzoyl, C₁-C₁₂alkanoyl, C₃-C₈cycloalkyl; or is substituted by phenyl optionally

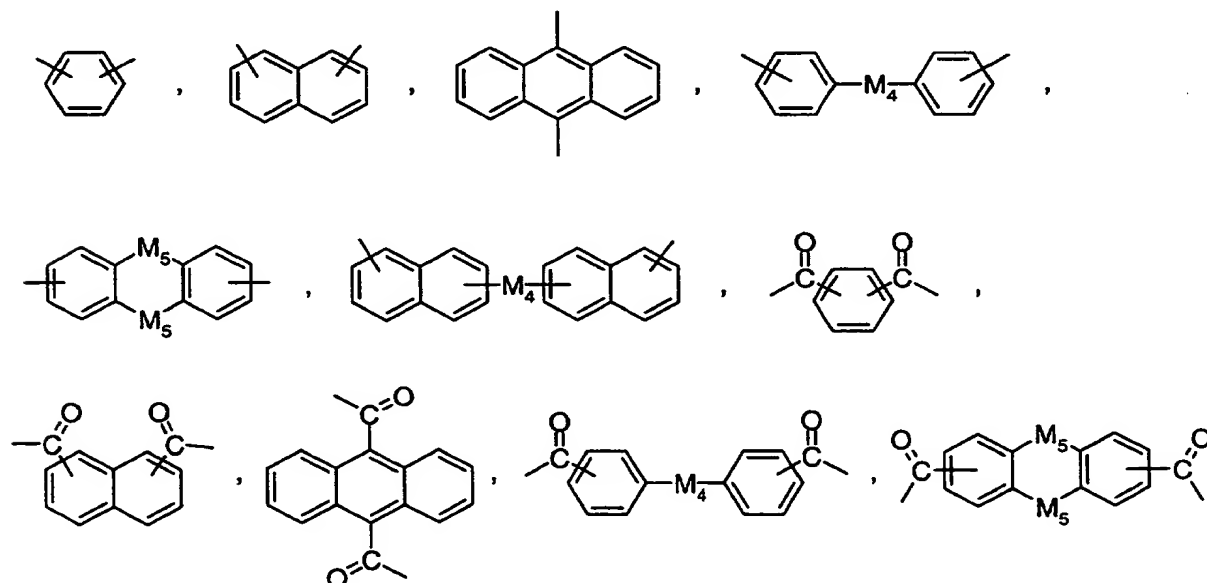
substituted by one or more OR_3 , SR_4 or NR_5R_6 ; or is substituted by C_2 - C_{12} alkoxycarbonyl optionally interrupted by one or more $-O-$ and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR_3 , SR_4 , SOR_4 , SO_2R_4 or NR_5R_6 , wherein the substituents OR_3 , SR_4 or NR_5R_6 optionally form 5- or 6-membered rings *via* the radicals R_3 , R_4 , R_5 and/or R_6 with further substituents on the aryl ring of the C_6 - C_{20} aryl or C_6 - C_{20} aryloyl group or with one of the carbon atoms of the aryl ring of the C_6 - C_{20} aryl or C_6 - C_{20} aryloyl group;

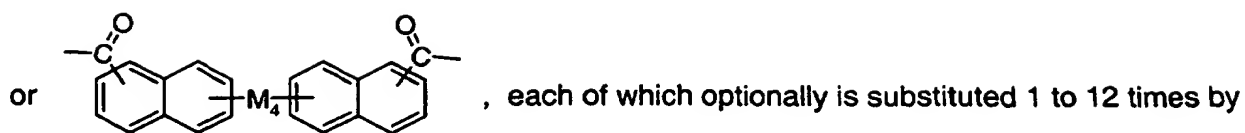
Ar_2 is either C_{10} - C_{20} aryl or C_{10} - C_{20} aryloyl,

each of these radicals is unsubstituted or substituted 1 to 12 times by halogen, C_1 - C_{12} alkyl, benzyl, benzoyl, C_1 - C_{12} alkanoyl, C_3 - C_8 cycloalkyl; or is substituted by phenyl optionally substituted by one or more OR_3 , SR_4 or NR_5R_6 ; or is substituted by C_2 - C_{12} alkoxycarbonyl optionally interrupted by one or more $-O-$ and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR_3 , SR_4 , SOR_4 , SO_2R_4 or NR_5R_6 , wherein the substituents OR_3 , SR_4 or NR_5R_6 optionally form 5- or 6-membered rings *via* the radicals R_3 , R_4 , R_5 and/or R_6 with further substituents on the aryl ring of the C_{10} - C_{20} aryl or the C_{10} - C_{20} aryloyl or with one of the carbon atoms of the aryl ring of the C_{10} - C_{20} aryl or the C_{10} - C_{20} aryloyl;

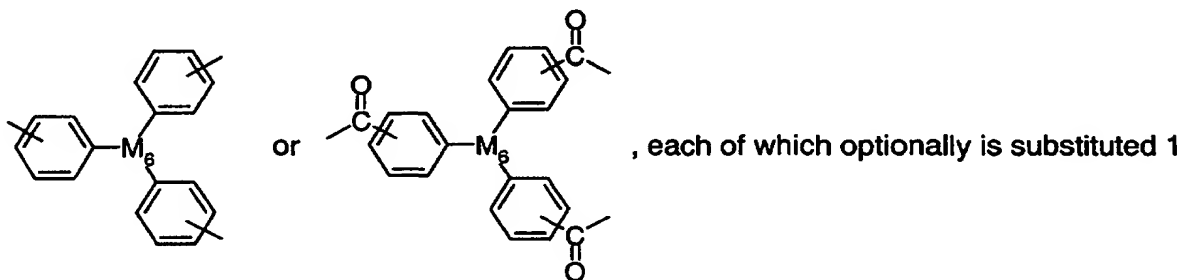
x is 2 or 3;

M_1 when x is 2, is a group



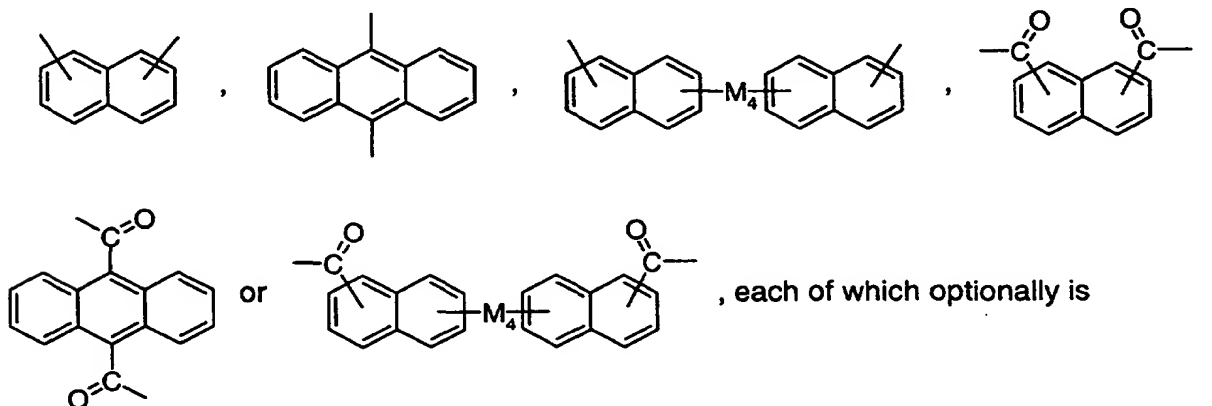


halogen, C₁-C₁₂alkyl, C₃-C₈cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR₃, SR₄ or NR₅R₆; enzy, benzoyl, C₁-C₁₂alkanoyl; C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆;
or M₁, when x is 3, is a group



to 12 times by halogen, C₁-C₁₂alkyl, C₃-C₈cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR₃, SR₄ or NR₅R₆; benzyl, benzoyl, C₁-C₁₂alkanoyl; C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR₃, SR₄, SOR₄, SO₂R₄ or NR₅R₆;

M₂ is a group



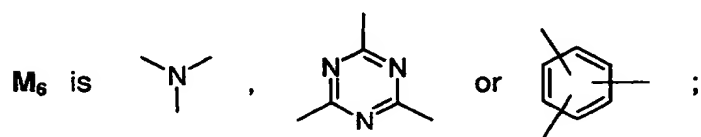
substituted 1 to 8 times by halogen, C₁-C₁₂alkyl, C₃-C₈cycloalkyl; phenyl which is unsubstituted or substituted by one or more OR₃, SR₄ or NR₅R₆; benzyl, benzoyl, C₁-C₁₂alkanoyl; C₂-C₁₂alkoxycarbonyl optionally interrupted by one or more -O- and/or

optionally substituted by one or more hydroxyl groups, phenoxycarbonyl or a group OR_3 , SR_4 , SOR_4 , SO_2R_4 or NR_5R_6 ;

M_3 is C_1 - C_{12} alkylene, cyclohexylene, phenylene, $-(\text{CO})\text{O}-(\text{C}_2-\text{C}_{12}\text{alkylene})-\text{O}(\text{CO})-$, $-(\text{CO})\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CO})-$ or $-(\text{CO})-(\text{C}_2-\text{C}_{12}\text{alkylene})-(\text{CO})-$;

M_4 is a direct bond, $-\text{O}-$, $-\text{S}-$, $-\text{SS}-$, $-\text{NR}_3-$, $-(\text{CO})-$, C_1 - C_{12} alkylene, cyclohexylene, phenylene, naphthylene, $-(\text{CO})\text{O}-(\text{C}_2-\text{C}_{12}\text{alkylene})-\text{O}(\text{CO})-$, $-(\text{CO})\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CO})-$ or $-(\text{CO})-(\text{C}_2-\text{C}_{12}\text{alkylene})-(\text{CO})-$; or M_4 is C_4 - C_{12} alkylene or C_4 - C_{12} alkylenedioxy-, each of which is optionally interrupted by 1 to 5 $-\text{O}-$, $-\text{S}-$ and/or $-\text{NR}_3-$;

M_5 is a direct bond, $-\text{CH}_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{SS}-$, $-\text{NR}_3-$ or $-(\text{CO})-$;



R_3 is hydrogen or C_1 - C_{12} alkyl; or R_3 is C_2 - C_6 alkyl which is substituted by $-\text{OH}$, $-\text{SH}$, $-\text{CN}$, C_1 - C_4 alkoxy, C_3 - C_6 alkenoxy, $-\text{OCH}_2\text{CH}_2\text{CN}$, $-\text{OCH}_2\text{CH}_2(\text{CO})\text{O}(\text{C}_1-\text{C}_4\text{alkyl})$, $-\text{O}(\text{CO})-\text{C}_1-\text{C}_4\text{alkyl}$, $-\text{O}(\text{CO})$ -phenyl, $-(\text{CO})\text{OH}$ or $-(\text{CO})\text{O}(\text{C}_1-\text{C}_4\text{alkyl})$; or R_3 is C_2 - C_6 alkyl which is interrupted by one or more $-\text{O}-$; or R_3 is $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, C_1 - C_8 alkanoyl, C_3 - C_{12} alkenyl, C_3 - C_6 alkenoyl, C_3 - C_8 cycloalkyl; or R_3 is benzoyl which is unsubstituted or substituted by one or more C_1 - C_6 alkyl, halogen, $-\text{OH}$ or C_1 - C_4 alkoxy; or phenyl which is unsubstituted or substituted by halogen, $-\text{OH}$, C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_3 is phenyl- C_1 - C_3 alkyl, $\text{Si}(\text{C}_1-\text{C}_6\text{alkyl})_r(\text{phenyl})_{3-r}$;

r is 0, 1, 2 or 3;

R_4 is hydrogen, C_1 - C_{12} alkyl, C_3 - C_{12} alkenyl, cyclohexyl; C_2 - C_6 alkyl which is substituted by $-\text{OH}$, $-\text{SH}$, $-\text{CN}$, C_1 - C_4 alkoxy, C_3 - C_6 alkenoxy, $-\text{OCH}_2\text{CH}_2\text{CN}$, $-\text{OCH}_2\text{CH}_2(\text{CO})\text{O}(\text{C}_1-\text{C}_4\text{alkyl})$, $-\text{O}(\text{CO})-\text{C}_1-\text{C}_4\text{alkyl}$, $-\text{O}(\text{CO})$ -phenyl, $-(\text{CO})\text{OH}$ or $-(\text{CO})\text{O}(\text{C}_1-\text{C}_4\text{alkyl})$; or R_4 is C_2 - C_{12} alkyl which is interrupted by one or more $-\text{O}-$ or $-\text{S}-$; or R_4 is phenyl which is unsubstituted or substituted by halogen, C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_4 is phenyl- C_1 - C_3 alkyl;

R_5 and R_6 independently of each other are hydrogen, C_1 - C_{12} alkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_{10} alkoxyalkyl, C_3 - C_5 alkenyl, C_3 - C_8 cycloalkyl, phenyl- C_1 - C_3 alkyl, C_1 - C_4 alkanoyl, C_3 - C_6 alkenoyl, benzoyl or phenyl which is unsubstituted or substituted by C_1 - C_{12} alkyl or C_1 - C_4 alkoxy; or R_5 and R_6 together are C_2 - C_6 alkylene optionally interrupted by $-\text{O}-$ or $-\text{NR}_3-$ and/or optionally substituted by hydroxyl, C_1 - C_4 alkoxy, C_2 - C_4 alkanoyloxy or benzoyloxy; provided that the compounds

1-naphthyl methyl ketone oxime-O-acetate, 2-naphthyl methyl ketone oxime-O-acetate, 2-naphthyl phenyl ketone oxime-O-propylcarbonate, 9-anthryl methyl ketone oxime-O-acetate, 2-naphthyl methyl ketone oxime-O-benzoate are excluded; and
(C) a photopolymerizable reactive and/or unreactive diluent.

2. Photosensitive composition according to claim 1, wherein component (B) is a compound of formula I, wherein

R₁ is C₁-C₈alkanoyl;

Ar₁ is C₆-C₁₄aryl which is unsubstituted or substituted by C₁-C₄alkyl, or OR₃, wherein the substituents OR₃, optionally form 5- or 6-membered rings *via* the radicals R₃ with further substituents on the aryl ring of the C₆-C₂₀aryl;

R₃ is C₁-C₄alkyl.

3. Photosensitive composition according to claim 1, wherein the oligomer or polymer (A) is a binder polymer, in particular a copolymer of (meth)acrylate and (meth)acrylic acid, or a resin obtained by the reaction of a saturated or unsaturated polybasic acid anhydride with a product of the reaction of an epoxy compound and an unsaturated monocarboxylic acid, or is an addition product formed between a carboxyl group-containing resin and an unsaturated compound having an α,β -unsaturated double bond and an epoxy group

4. Photosensitive composition according to claim 1 additionally comprising an epoxy compound which contains at least two epoxy groups in the molecule.

5. Photosensitive composition according to claim 1, which additionally to the components (A), (B) and (C) comprises at least one photosensitizer compound (D), and/or further additives (E).

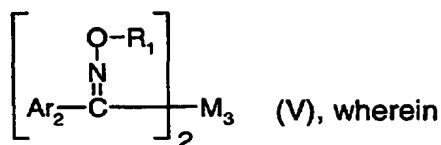
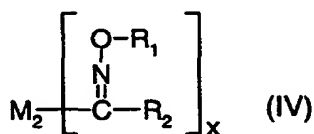
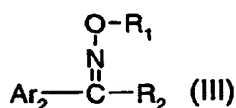
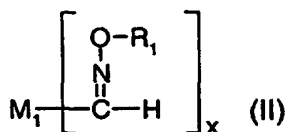
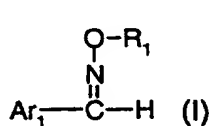
6. Photosensitive composition according to claim 5, comprising further additives (E), which are selected from the group consisting of inorganic fillers, colourants, epoxy curing agents, thermal polymerization inhibitors, thickeners, antifoaming agents and leveling agents, in particular inorganic fillers.

7. Photosensitive composition according to claim 5, comprising 100 parts by weight of component (A), 0.015 to 60 parts by weight of component (B), 5 to 300 parts by weight of component (C) and 0.015 to 60 parts by weight of component (D).
8. Solder resist comprising a composition according to anyone of claims 1-7.
9. Process for the photopolymerization of compounds containing ethylenically unsaturated double bonds, which comprises irradiating a composition according to anyone of claims 1-7 with electromagnetic radiation in the range from 190 to 600 nm.
10. Coated substrate which is coated on at least one surface with a composition according to anyone of claims 1-7.
11. Process for the photographic production of relief images, wherein a coated substrate according to claim 10 is subjected to imagewise exposure with electromagnetic radiation in the range from 190 to 600 nm, and then the unexposed portions are removed with a solvent.
12. A color filter prepared by providing red, green and blue (RGB) colour elements and, optionally a black matrix, all comprising a photosensitive composition according to anyone of claims 1-7 and a pigment on a transparent substrate and providing a transparent electrode either on the surface of the substrate or on the surface of the color filter layer.
- 13 Process for forming images, wherein
 - (1) the components of a composition according to anyone of claims 1-7 are mixed,
 - (2) the resulting composition is applied to the substrate,
 - (3) the solvent, if present, is evaporated, at elevated temperature,
 - (4) the coated substrate is exposed to irradiation through a negative mask,
 - (5) the irradiated sample is developed, by washing with aqueous alkaline solution and thereby removing the uncured areas and
 - (6) the sample is thermally cured.

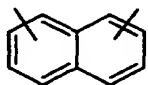
Abstract

Photosensitive compositions comprising

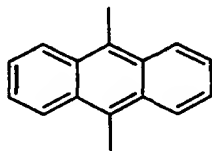
- (A) an oligomer or polymer containing at least one carboxylic acid group in the molecule;
 (B) at least one compound of formula I, II, III, IV or V



R_1 inter alia is C_4 - C_9 cycloalkanoyl, C_3 - C_{12} alkenoyl, or benzoyl which is unsubstituted or substituted; R_2 is for example phenyl which is unsubstituted or substituted, C_2 - C_{12} alkoxycarbonyl, phenoxycarbonyl; Ar_1 and Ar_2 are either C_6 - C_{20} aryl or C_6 - C_{20} aryloyl each of which is unsubstituted or substituted; x is 2 or 3; M_1 , when x is 2, inter alia is a group

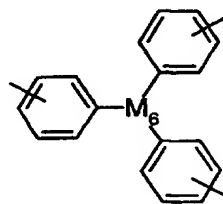


, or



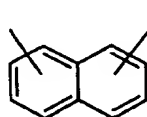
, each of which optionally is

substituted; or M_1 , when x is 3, is for example a group

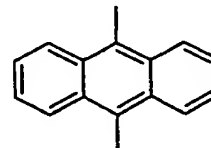


, optionally

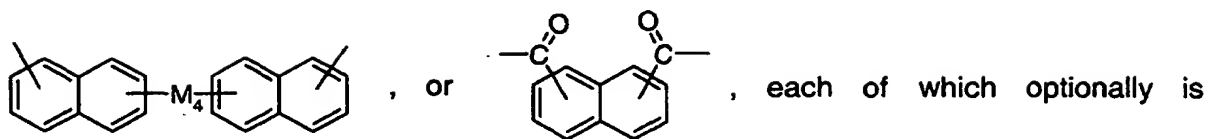
substituted; M_2 inter alia is a group



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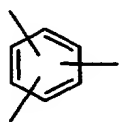
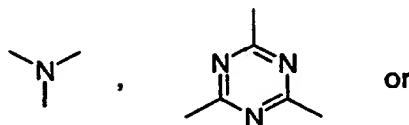


,



substituted; M_4 is for example a direct bond, -O-, -S-, -SS-, -NR₃-, -(CO)-, C₁-C₁₂alkylene,

cyclohexylene, phenylene, or naphthylene; M_6 is



; R_3 is for example hydrogen or C₁-C₁₂alkyl; C₂-C₆alkyl which is for example

substituted by -OH, -SH, -CN, C₁-C₄alkoxy, C₃-C₆alkenoxy, or -OCH₂CH₂CN; R_4 is for example hydrogen, C₁-C₁₂alkyl, C₃-C₁₂alkenyl, cyclohexyl, or phenyl which is unsubstituted or substituted; R_5 and R_6 independently of each other inter alia are hydrogen, C₁-C₁₂alkyl, C₂-C₄hydroxyalkyl, C₂-C₁₀alkoxyalkyl, C₃-C₅alkenyl, C₃-C₈cycloalkyl, phenyl-C₁-C₃alkyl, C₁-C₄alkanoyl, C₃-C₆alkenoyl, benzoyl or phenyl which is unsubstituted or substituted; and (C) a photopolymerizable reactive and/or unreactive diluent.

exhibit an unexpectedly good performance, in particular in photoresist technology.